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THE *B*-STATE OF THE HYDROGEN MOLECULE

By Clarence Zener and Victor Guillemin, Jr.
Jefferson Physical Laboratory, Harvard University

(Received August 29, 1929)

Abstract

An attempt has been made to develop a wave function for the *B*-state of the H_2 molecule using the variation method. The procedure adopted was only partially successful as indicated by the discrepancy between the computed energy of dissociation 2.64 volts and the value obtained from band spectrum data, viz., 3.37 volts. The form of the wave-function indicates that the *B*-state is partially, but not wholly polar.

Incidentally a method has been developed for the integration of

$$\int_1^\infty d\lambda_1 \int_1^\infty d\lambda_2 Q_\tau \binom{\lambda_1}{\lambda_2} P_\tau \binom{\lambda_2}{\lambda_1} \lambda_1^m \lambda_2^n e^{-\alpha_1\lambda_1-\alpha_2\lambda_2}, \quad \binom{\lambda_1>\lambda_2}{\lambda_2>\lambda_1}$$

an integral occurring in

$$\int \psi(1/r_{12})\psi dV.$$

when elliptic coordinates are used.

I. Introduction

Dieke and Hopfield[1] have shown that the Lyman and Werner bands appear in the absorption spectrum of normal hydrogen as well as in the emission spectrum. The upper states for these two systems, called *B* and *C* respectively, apparently dissociate adiabatically into a normal and a two-quantum hydrogen atom and are accordingly called two-quantum states. The corresponding band systems, due to transitions to the normal state *A*, are the Werner bands, $C-A$ and the Lyman bands $B-A$.

The *C*-state has been investigated by Kemble and Zener[2] by a perturbation method. In the present paper the *B*-state is treated by a variation method similar to that used by Wang[3] for the *A*-state. This type of analysis has been used successfully by the authors[4] in calculating the potential energy curve for the H_2^+ ion.

[1] G. H. Dieke and J. J. Hopfield, Phys. Rev. **30**, 400 (1927).
[2] E. C. Kemble and C. Zener, Phys. Rev. **33**, 512 (1929).
[3] S. C. Wang, Phys. Rev. **31**, 579 (1928).
[4] V. Guillemin, Jr., and C. Zener, Proc. Nat. Acad. Sci. **15**, 314 (1929).

It depends essentially on the proposition that the correct wave function ψ of a system with Hamiltonian H will give, for the energy integral[5]

$$J=\frac{\int \psi H\overline{\psi}dV}{\int \psi\overline{\psi}dV} \tag{1}$$

a set of stationary values which are the proper energy values for the system. The correct ψ being unknown, an approximate function

$$\psi(\alpha_1,\alpha_2,\cdots,)$$

is guessed at, and the arbitrary parameters α_1, α_2, $\cdots$ are so adjusted as to make J an extremal. This procedure yields the best wave function and the best energy values consistent with the type of function assumed to begin with.

In the H_2^+ problem the above method was used to obtain the energy of the normal state (absolute minimum of J), but it is applicable as well to all excited states which are the lowest of their particular symmetry characteristics.

The B-state is the lowest of the S^EA^N type,[6] e.g. symmetrical in the electrons, antisymmetrical in the nuclei, and can therefore be treated by the same procedure as was used for the ion. It is a particularly interesting state to consider since one does not know definitely whether it is polar or non-polar in character. It has been found possible to make the following analysis sufficiently general to include both kinds of wave functions so that no arbitrary decision need be made at the start.

The form of wave function to be used for the molecule is chosen with the aid of the well-known device of carrying the nuclei adiabatically from their equilibrium distance $R=R_0$ to $R=0$ and $R=\infty$. At $R=0$ (helium) we note the following:

1. Detailed analysis of the $B-A$ bands[7] shows that the B state is a $^1\Sigma$ state (Hund's new notation). Hence the helium state obtained from it at $R=0$ has zero angular momentum in the direction of the internuclear axis. Introducing the usual spherical coordinates ρ, θ, ϕ with the internuclear line as an axis, this leads to the requirement that in the limiting case of zero electronic interaction the helium wave functions shall be independent of the azimuthal angles ϕ_1 and ϕ_2 of the two electrons.

2. The S^E symmetry requires that the function be symmetrical with respect to an interchange of the coordinates of the electrons. Hence in the limiting case of zero electronic interaction the wave function must be of the form

[5] This integral, and all the following, are understood to be extended over all of the $3n$-dimensional space of the n particles of the system unless otherwise indicated.

[6] For the notation see Kemble and Zener, reference 2, p. 516.

[7] E. C. Kemble and V. Guillemin, Jr., Proc. Nat. Acad. Sci. **14**, 782, (1928).

$$\psi = \psi_{12} + \psi_{21}$$

where

$$\psi_{ij}=\psi_\alpha(\rho_i,\theta_i)\psi_\beta(\rho_j,\theta_j)$$

and ψ_α, ψ_β are hydrogenic wave functions.

3. The low energy of the B-state requires that one of the two functions ψ_α, ψ_β shall be the nodeless function characteristic of the normal state of He.

4. The A^N symmetry requires that the other factor say ψ_β, shall involve a Legendre polynomial in $\cos\theta$ of odd degree.

The wave functions for the lowest energy levels corresponding to these conditions are, neglecting the normalizing factor and using $a_H=0.532\times10^{-8}$cm as the unit of length,

$$1s2p\,^1P:\quad \psi_{ij}=\rho_j\cos\theta_j e^{-(2\rho_i+\rho_j)} \tag{2}$$

and

$$1s3p\,^1P:\quad \psi_{ij}=\rho_j(\rho_j-6)\cos\theta_j e^{-(2\rho_i+2\rho_j/3)}. \tag{3}$$

When we now change adiabatically to $R=\infty$, the cosine factor in (2) defines a nodal plane midway between the two nuclei. If we keep one electron with each nucleus we have two atoms in the normal state (no nodes) where the A^N symmetry necessarily means A^E as well. Therefore, the desired S^EA^N symmetry is possible only if both electrons are on one nucleus at the same time, that is, (2) necessarily separates into ions, giving

$$\psi_{ij}=e^{-(\rho_{ai}+\rho_{aj})}-e^{-(\rho_{bi}+\rho_{bj})} \tag{2'}$$

where ρ_{ai} and ρ_{bi} are the distances of electron i from nucleus a and nucleus b respectively. (3) goes over into

$$\psi_{ij}=(\zeta-2)e^{-(\rho_{ai}+\rho_{bj}/2)}-(\zeta-2)e^{-(\rho_{bi}+\rho_{aj}/2)} \tag{3'}$$

that is, one normal and one two quantum excited H atom. The spherical node in (3) has gone over into a pair of paraboloidal nodes given by the parabolic coordinate ζ.

In order to set up functions which will interpolate between (2), (2′) and (3), (3′) respectively, we adopt the elliptic coordinates

$$\lambda_i=\frac{\rho_{ai}+\rho_{bi}}{R},\qquad \mu_i=\frac{\rho_{ai}-\rho_{bi}}{R}$$

as the natural intermediary between spherical and parabolic coordinates. The required functions are of the form:

$$\psi_{ij}=\lambda_j e^{-(\alpha_n\lambda_i+\alpha_e\lambda_j)}\left[e^{+(\beta_n\mu_i+\beta_e\mu_j)}-e^{-(\beta_n\mu_i+\beta_e\mu_j)}\right] \tag{2''}$$

$$\psi_{ij}=\lambda_j(\lambda_j+\gamma)e^{-(\alpha_n\lambda_i+\alpha_e\lambda_j)}\left[e^{(\beta_n\mu_i+\beta_e\mu_j)}-e^{-(\beta_n\mu_i+\beta_e\mu_j)}\right] \tag{3''}$$

The changes in the coefficients of the ρ's between (2) (3) and (2′) (3′) have been taken care of by the variable parameters α and β. Two separate parameters are used with λ and μ to obtain greater flexibility. The subscript

n refers to the normal, e to the excited state. A third parameter γ determines the position of the node. The β's are of the form: $\beta = R \cdot \beta'(R)$, where $\beta'(R)$ is finite for the whole range $0 \leq R < \infty$. Therefore, if we stipulate that $\beta_n \ll \beta_e$ as $R \to 0$, the function of μ becomes $2\beta_e \mu_j$ at $R \to 0$. But

$$\lim_{R \to 0} \mu_j = \cos \theta_j$$

which gives the required cosine factor in (2) and (3). The first factor ρ in (2) and (3) has disappeared in (2′) and (3′). This change is effected by (2″) and (3″) where λ is substituted for ρ. For as $R \to 0$, $\frac{1}{2}R \cdot \lambda \to \rho$; while as $R \to \infty$, $\lambda \to 1$ near the nucleus, i.e., the factor λ is constant wherever ψ is non-vanishing.[8]

It is obvious, therefore, that (2″) and (3″) will afford the required interpolation between (2), (2′) and (3), (3′). However, (2″) is a special case of (3″) for $\gamma = \infty$. Therefore (3″), with suitable values of the parameter, should be an approximate solution for the exact Hamiltonian at all values of R both where it is polar and where it is non-polar.

In the following we are interested only in finding the function and the energy value at the equilibrium distance $R = R_0$. We therefore sacrifice the ability of ψ to carry over into the helium function (3) by omitting the first λ factor in (3″). This not only simplifies the analysis, but will actually improve the approximation if, as we shall later verify, γ is positive. The wave function used in the following analysis will therefore be:

$$\begin{aligned}\psi = {} & (\lambda_j + \gamma) e^{-(\alpha_n \lambda_i + \alpha_e \lambda_j)} \left[e^{(\beta_n \mu_i + \beta_e \mu_j)} - e^{-(\beta_n \mu_i + \beta_e \mu_j)} \right] \\ & + (\lambda_i + \gamma) e^{-(\alpha_n \lambda_j + \alpha_e \lambda_i)} \left[e^{(\beta_n \mu_j + \beta_e \mu_i)} - e^{-(\beta_n \mu_j + \beta_n \mu_i)} \right].\end{aligned} \tag{4}$$

In terms of this function we can now state definitely what is to be understood by a polar or non-polar molecule. If β_n and β_e are of like sign and $\gamma > 0$ (no node in λ) the function is polar, while if β_n and β_e are of opposite sign and $\gamma < 0$ it is non-polar. Thus, when the values of the parameters have been derived from the variation principle one should have not only a quantitative determination of the energy but qualitative information about the type of molecule involved as well.

Anticipating the results, it may be stated that the outcome of the analysis is not entirely unambiguous: the energy is found to depend only very slightly upon the sign of β_n relative to β_e. This would indicate that, at the equilibrium value of R at which the calculations are made, the molecule is neither polar nor non-polar, but a combination of the two.

II. Method

The parameters in the function (4) are to be determined from the variation principle

[8] Any *constant* coefficient (including zero and infinity) appearing in any of these transformations is, of course, of no moment since it appears in both numerator and denominator of (1).

$$\delta J = 0 \tag{5}$$

(the variation being taken with respect to the parameters) and the values so obtained are to be introduced into (1) to obtain the energy value.

The Hamiltonian of the molecule is:

$$H = -(\Delta_1^* + \Delta_2^*) + \frac{2}{\rho_{12}} + \frac{2}{R}.$$

Here ρ_{12} is the distance between the electrons and

$$\Delta_i^* = \Delta_i + \frac{2}{\rho_{ai}} + \frac{2}{\rho_{bi}}$$

Δ_i being the Laplacian operator.

In order that identical terms in J may be collected, ψ is written in the symmetrical form

$$\psi = G(\phi^1{}_n\phi^2{}_e - \phi^1{}_{-n}\phi^2{}_{-e} + \phi_n{}^2\phi_e{}^1 - \phi^2{}_{-n}\phi^1{}_{-e}) \tag{6}$$

where

$$\phi^i{}_{\pm n} = e^{-(\alpha_n\lambda_i \pm \beta_n\mu_i)}\ ;\ \phi^i{}_{\pm e} = (\lambda_i + \gamma)e^{-(\alpha_e\lambda_i \pm \beta_e\mu_i)}.$$

Here the normalizing factor G has been introduced explicitly. Then, since H is invariant to the transformations

$$\begin{gathered}\lambda_1, \mu_1 \rightarrow \lambda_2, \mu_2 \\ \mu_1 \rightarrow -\mu_1,\ \ \mu_2 \rightarrow -\mu_2\end{gathered} \tag{7}$$

J may be written

$$J = 4G^2(H_{12}{}^{12} - H_{-12}{}^{12} + H_{21}{}^{12} - H_{-21}{}^{12}) \tag{8}$$

where

$$H_{\pm lm}{}^{ij} = \int \phi_{\pm n}{}^l\phi_{\pm e}{}^m H\phi_n{}^i\phi_e{}^j dV. \tag{9}$$

In elliptic coordinates[9]

$$\Delta_i^* = \frac{4}{R^2(\lambda_i{}^2 - \mu_i{}^2)}\left[\frac{\partial}{\partial\lambda_i}(\lambda_i{}^2 - 1)\frac{\partial}{\partial\lambda_i} + \frac{\partial}{\partial\mu_i}(1 - \mu_i{}^2)\frac{\partial}{\partial\mu_i} + 2R\right] \tag{10}$$

length being expressed in units of a_H and energy in units of $E_H = 2\pi^2 me^4/h^2$.

Neumann's expansion of $1/\rho_{12}$[10] is used. The only terms that do not vanish upon integration with respect ϕ_1, ϕ_2 are

$$\frac{1}{\rho_{12}} = \frac{2}{R}\sum_{\tau=0}^{\infty}(2\tau+1)P_\tau\begin{pmatrix}\lambda_1\\ \lambda_2\end{pmatrix}Q_\tau\begin{pmatrix}\lambda_2\\ \lambda_1\end{pmatrix}P_\tau(\mu_1)P_\tau(\mu_2). \tag{11}$$

Where the upper variables are to be used when $\lambda_2 > \lambda_1$, the lower when $\lambda_1 > \lambda_2$.

[9] Guillemin and Zener, reference 4, Eq. (3).

[10] Kemble and Zener, reference 2, Eq. (32).

All the integrals which occur in J may be reduced to the three types

$$A_n(\alpha) = \int_1^\infty \lambda^n e^{-\alpha\lambda} d\lambda \tag{12}$$

$$B_n(\alpha) = \int_{-1}^1 \lambda^n e^{-\alpha\lambda} d\lambda \tag{13}$$

$$\begin{aligned} H_\tau(m,\alpha_1,n,\alpha_2) &= \int_1^\infty d\lambda_1 \int_1^\infty d\lambda_2 Q_\tau\begin{pmatrix}\lambda_1\\ \lambda_2\end{pmatrix} P_\tau\begin{pmatrix}\lambda_2\\ \lambda_1\end{pmatrix} \cdot \lambda_1{}^m \lambda_2{}^n e^{-\alpha_1\lambda_1-\alpha_2\lambda_2} \\ &= \int_1^\infty d\lambda_j\, Q_\tau(\lambda_j)\lambda_j{}^m e^{-\alpha_1\lambda_j} \int_1^{\lambda_j} P_\tau(\lambda_i)\lambda_i{}^n e^{-\alpha_2\lambda_i} d\lambda_i \\ &\quad + \int_1^\infty d\lambda_j Q_\tau(\lambda_j)\lambda_j{}^n e^{-\alpha_2\lambda_j} \int_1^{\lambda_j} P_\tau(\lambda_i)\lambda_i{}^m e^{-\alpha_1\lambda_i} d\lambda_i . \end{aligned} \tag{14}$$

The simplest of these is (12). For future use however we shall consider a more general type of integral:

$$A_n(\sigma,\alpha) = \int_\sigma^\infty \lambda^n e^{-\alpha\lambda} d\lambda \tag{12'}$$

of which (12) is the special case $\sigma = 1$. By integration by parts, we immediately get the recurrence formula:

$$A_n(\sigma,\alpha) = \frac{\sigma^n e^{-\sigma\alpha}}{\alpha} + \frac{n}{\alpha} A_{n-1}(\sigma,\alpha) \tag{15}$$

from which we obtain the series solution:

$$A_n(\sigma,\alpha) = \frac{e^{-\sigma\alpha}}{\alpha} \sum_{\nu=0}^{n} \frac{n!}{(n-\nu)!} \frac{\sigma^{n-\nu}}{\alpha^\nu} . \tag{16}$$

Integrating by parts again we obtain the recurrence relation for (13)

$$B_n(\alpha) = \frac{1}{\alpha}[(-1)^n e^\alpha - e^{-\alpha}] + \frac{n}{\alpha} B_{n-1}(\alpha) . \tag{17}$$

In the successive application of this formula we alternately add positive and negative terms. When α is small, say $|\alpha| < 1$, and n is large, these terms nearly cancel so that the formula is not satisfactory for numerical computation. However, in this range of α, the integration in series, after expanding the exponential, converges very well. Thus, from

$$B_n(\alpha) = \int_{-1}^1 \lambda^n \sum_{\nu=0}^{\infty} (-1)^\nu \frac{(\alpha\lambda)^\nu}{\nu!} d\lambda$$

we obtain

$$B_n(\alpha)=2\sum_{\nu=0}^{\infty}\frac{\alpha^{2\nu}}{(2\nu)!(2\nu+n+1)} \quad \text{for } n \text{ even}$$
$$=-2\sum_{\nu=0}^{\infty}\frac{\alpha^{2\nu+1}}{(2\nu+1)!(2\nu+n+2)} \quad \text{for } n \text{ odd}. \tag{18}$$

From (17) or (18) $B_n(\alpha)$ may be conveniently calculated for any value of α.

The integral (14) is much more difficult to reduce to a suitable form for numerical calculation. It would be possible, of course, to expand $Q_\nu(\lambda)$ in an inverse power series in λ, but this does not converge sufficiently well to be useful for numerical computation. The following reduction is rather tedious but does give a form from which numerical values may be readily calculated. We first consider the integral

$$f_\nu(m,\alpha)=\int_1^\infty \lambda^m e^{-\alpha\lambda}Q_\nu(\lambda)d\lambda. \tag{19}$$

Since

$$Q_0(\lambda)=\frac{1}{2}\ln\left(\frac{\lambda+1}{\lambda-1}\right), \quad \lambda>1$$
$$f_0(m,\alpha)=\lim_{\epsilon\to 0}\frac{1}{2}\int_{1+\epsilon}^{\infty}\lambda^m e^{-\alpha\lambda}\ln\left(\frac{\lambda+1}{\lambda-1}\right)d\lambda. \tag{19'}$$

Integrating by parts and using elation (16) we get

$$f_0(m,\alpha)=\lim_{\epsilon\to 0}\frac{1}{2}\Bigg\{(\ln 2-\ln\epsilon)A_m(1,\alpha)$$
$$+\frac{1}{\alpha}\int_{1+\epsilon}^{\infty}\sum_{\nu=0}^{m}\frac{m!}{(m-\nu)!}\frac{e^{-\alpha\lambda}\lambda^{m-\nu}}{\alpha^\nu}\left(\frac{1}{\lambda+1}-\frac{1}{\lambda-1}\right)d\lambda\Bigg\} \tag{20}$$

In the second term of (20) we make the substitutions

$$x=\lambda+1, \qquad y=\lambda-1$$

and note that

$$e^{-\alpha\lambda}\sum_{\nu=0}^{m}\lambda^{m-\nu}=e^{\alpha}\sum_{\nu=0}^{m}\sum_{s=0}^{m-\nu}(-1)^{m-\nu-s}\binom{m-\nu}{s}x^s e^{-\alpha x}$$
$$=e^{-\alpha}\sum_{\nu=0}^{m}\sum_{s=0}^{m-\nu}\binom{m-\nu}{s}y^s e^{-\alpha y}$$

Passing to the limit, and using (16) gives

$$f_0(m,\alpha)=\tfrac{1}{2}[(\ln 2\,\alpha+C)A_m(1,\alpha)-E_i(-2\alpha)\mathrm{A}_m(-1,\alpha)]-\theta_0(m,\alpha) \tag{21}$$

where

$$\theta_0(m,\alpha)=-\frac{1}{2}\frac{e^{-\alpha}}{\alpha}\sum_{\nu=0}^{m}\sum_{s=1}^{m-\nu}\frac{m!}{(m-\nu)!}\binom{m-\nu}{s}\frac{1}{\alpha^{\nu}}\left[(-1)^{m-\nu-s-1}\sum_{k=0}^{s-1}\frac{(s-1)!}{(s-k-1)!}\frac{2^{s-k-1}}{\alpha^{k+1}}-\frac{(s-1)!}{\alpha^{s}}\right] \tag{22}$$

The symbol E_i stands for the integral logarithm:[11]

$$E_i(x)=\int_{\infty}^{-x}e^{-\lambda}d\lambda/\lambda. \tag{23}$$

We have made use of (23) and of the equation

$$E_i(-\epsilon\alpha)=C+\ln|\epsilon\alpha|-\epsilon\alpha+\tfrac{1}{4}(\epsilon\alpha)^{21}-\cdots$$

where $C=$ Euler's constant $=0.577216$.

It is to be observed that (22) is of the form

$$\theta_0(m,\alpha)=\frac{e^{-\alpha}}{\alpha}\sum_{\nu=0}^{m}C_{\nu}^{0m}\alpha^{-\nu} \tag{24}$$

where the C_{ν}^{0m}'s are numerical coefficients. These coefficients may be readily determined by a recurrence relation. This relation is obtained by substituting (21), (24) into

$$\frac{\partial}{\partial\alpha}f_0(m,\alpha)=-f_0(m+1,\alpha)$$

a formula which may be verified from (19). Use is made of

$$\frac{\partial}{\partial\alpha}A_m(\sigma,\alpha)=-A_{m+1}(\sigma,\alpha)\ ;\quad\frac{\partial}{\partial\alpha}E_i(-2\alpha)=\frac{e^{-2\alpha}}{\alpha}.$$

Equating the coefficients of $\alpha^{-\nu}$ gives the desired relation

$$\begin{cases}C_{\nu}^{0m+1}=C_{\nu}^{0m}+\nu C_{\nu-1}^{0m}+\dfrac{[1-(-1)^{m-\nu}]}{2}\dfrac{m!}{(m-\nu)!}, & 0<\nu\leq m\\ C_0^{0m+1}=C_0^{0m}\end{cases} \tag{25}$$

A list of C_{ν}^{0n} is given in Table I.

TABLE I. *Values of* C_{ν}^{0n}.

n	$\nu=0$	1	2	3	4	5	6	7
0	0							
1	0	0						
2	0	1	0					
3	0	1	4	0				
4	0	2	6	18	0			
5	0	2	14	36	96	0		
6	0	3	18	98	240	600	0	
7	0	3	30	152	752	1800	4320	0
8	0	4	36	284	1360	6400	15120	35280

[11] E. Jahnke and F. Emde: Funktionentafeln, G. B. Teubner, Berlin, p. 19.

Having completed the evaluation of $f_0(m,\alpha)$, we now return to the complete integral $H_0(m, \alpha_1, n, \alpha_2)$ as defined by (14). Since $P_0(\alpha)=1$, the integration with respect to λ_i is of the form given by (12′).[12]

Performing this integration and applying definition (19′) we obtain

$$H_0(m,\alpha_1,n,\alpha_2)=A_m(1,\alpha_1)f_0(n,\alpha_2)+A_n(1,\alpha_2)f_0(m,\alpha_1)$$
$$-\left[\sum_{\nu=0}^{m}e^{\alpha_1}A_\nu(1,\alpha_1)+\sum_{\nu=0}^{n}e^{\alpha_2}A_\nu(1,\alpha_2)\right]f_0(m+n-\nu,\alpha_1+\alpha_2). \quad (26)$$

That portion of $H_0(m, \alpha_1, n, \alpha_2)$ which does not contain the functions $\theta_0(m, \alpha)$ as factors may be further simplified. This portion is separated by the definition

$$H_0(m,\alpha_1,n,\alpha_2)=H_0^1(m,\alpha_1,n,\alpha_2)+H_0^2(m,\alpha_1,n,\alpha_2) \quad (27)$$

where

$$H_0^1(m,\alpha_1,n,\alpha_2)=-A_n(1,\alpha_2)\theta_0(m,\alpha_1)-A_m(1,\alpha_1)\theta_0(n,\alpha_2)$$
$$+\left\{\sum_{\nu=0}^{n}\frac{n!}{(n-\nu)!\alpha_2^{\nu+1}}+\sum_{\nu=0}^{m}\frac{m!}{(m-\nu)!\alpha_1^{\nu+1}}\right\}\theta_0(m+n-\nu,\alpha_1+\alpha_2) \quad (28)$$

and

$$H_0^2(m,\alpha_1,n,\alpha_2)=\frac{1}{2}\left[A_m(1,\alpha_1)A_n(1,\alpha_2)\left(\ln\frac{2\alpha_1\alpha_2}{\alpha_1+\alpha_2}+C\right)\right.$$
$$-A_m(-1,\alpha_1)A_n(1,\alpha_2)E_i(-2\alpha_1)-A_m(1,\alpha_1)A_n(-1,\alpha_2)E_i(-2\alpha_2)$$
$$\left.+A_m(-1,\alpha_1)A_n(-1,\alpha_2)E_i\{-2(\alpha_1+\alpha_2)\}\right] \quad (29)$$

In (29) we have used the transformation

$$\left[\sum_{\nu=0}^{m}e^{\alpha_1}A_\nu(1,\alpha_1)+\sum_{\nu=0}^{n}e^{\alpha_2}A_\nu(1,\alpha_2)\right]A_{m+n-\nu}(\sigma,\alpha_1+\alpha_2)$$
$$=\int_\sigma^\infty d\lambda_2\lambda_2{}^n e^{-\alpha_2\lambda_2}\int_{\lambda_2}^\infty\lambda_1{}^m e^{-\alpha_1\lambda_1}d\lambda_1+\int_\sigma^\infty d\lambda_1\lambda_1{}^m e^{-\alpha_1\lambda_1}\int_{\lambda_1}^\infty\lambda_2{}^n e^{-\alpha_2\lambda_2}d\lambda_2$$
$$=\int_\sigma^\infty\lambda_1{}^m e^{-\alpha_1\lambda_1}d\lambda_1\int_\sigma^\infty\lambda_2{}^n e^{-\alpha_2\lambda_2}d\lambda_2=A_m(\sigma,\alpha_1)A_n(\sigma,\alpha_2). \quad (30)$$

The procedure for $\tau=1, 2, 3, \cdots$ is very similar to that for $\tau=0$. Writing $Q_\tau(\lambda)$ in the form[13]

$$Q_\tau(\lambda)=\sum_{s=0}^{\tau}q_\tau{}^s\lambda^s Q_0(\lambda)+\text{polynomial in }\lambda$$

the expression for $f_\tau(m, \alpha)$ becomes

$$f_\tau(m,\alpha)=\frac{1}{2}\sum_{s=0}^{\tau}q_\tau{}^s[(\ln 2\alpha+C)A_{m+s}(1,\alpha)-E_i(-2\alpha)A_{m+s}(-1,\alpha)]-\theta_\tau(m,\alpha) \quad (21')$$

[12] Since $\int_1^\lambda\lambda_i{}^n e^{-\alpha\lambda_i}d\lambda_i=A_n(1,\alpha)-A_n(\lambda,\alpha)$.

[13] Compare: E. Madelung, Math. Hilfsmittel d. Physikers, J. Springer, Berlin. (1925), p. 59, Ed. 2.

where

$$\theta_\tau(m,\alpha)=\frac{e^{-\alpha}}{\alpha}\sum_{\nu=0}^{m+\tau}C_\nu{}^{\tau\,m}\alpha^{-\nu}.$$

The numerical coefficients $C_\nu{}^{\tau m}$ have recurrence relations both in m and in τ, namely

$$C_\nu{}^{\tau\ m+1}=C_\nu{}^{\tau\ m}+\nu C_{\nu-1}^{\tau m}+\sum_{s=0}^{\tau}\frac{q_\tau{}^s[1-(-1)^{m+s-\nu}](m+s)!}{2(m+s-\nu)!}\ ;\ \nu>0 \qquad (25')$$

$$C_0{}^{\tau\ m+1}=C_0{}^{\tau\ m}$$

and

$$C_\nu{}^{\tau+1\ m}=\frac{1}{\tau+1}\left\{(2\tau+1)C_\nu{}^{\tau\ m+1}-\tau\,C_\nu{}^{\tau-1\ m}\right\}\ ;\ \tau>1 \qquad (31)$$

$$C_\nu{}^{1\ m}=C_\nu{}^{0\ m+1}-\frac{m!}{(m-\nu)!}\,.$$

As for the rest of the analysis, we note that the integral

$$\int_1^\lambda \lambda^m e^{-\alpha\lambda}P_\tau(\lambda)d\lambda$$

is merely a linear combination of integrals of the type

$$\int_1^\lambda \lambda^m e^{-\alpha\lambda}d\lambda$$

with increasing values of m. Thus we have, in effect, not one but several values of m and n, and the resulting expression for $H_\tau(m, \alpha_1, n, \alpha_2)$differs from (26) in that every function of m and n is correspondingly replaced by a linear combination of several such functions with different m and n values.

The actual process of minimizing J with respect to the five parameters α_n, α_e, β_n, β_e, γ was carried through for the equilibrium distance $R_0\sim 2.5\alpha_H$[14] It was done by plotting sets of curves showing J as a function of each parameter separately. The computation was by cut and try methods. In some cases probable values of the parameters were guessed at as a starting point for the determination, in others certain parameters were set equal to zero in order to simplify the calculations with the others. (The latter procedure is always justified when the percent change in J due to a change in any one parameter from zero to its correct value is small, since the error introduced into the determination of a second parameter is small of the second order.)

The work was greatly facilitated by the comparative ease with which the slopes of the function with respect to any one of the parameters can be calculated. This is due to the fact that all the integrals in question are not

[14] Kemble and Zener, reference 2, Fig. 1.

changed in form by differentiating with respect to any one of the parameters. Thus, from (12′) it follows that

$$\frac{\partial}{\partial\alpha}A_n(\sigma,\alpha)=-A_{n+1}(\sigma,\alpha),$$

and similar relations hold for the integrals (13) and (14).

As stated above, the outcome of the analysis, as far as a qualitative decision between the polar or non-polar type of molecule is concerned, is not decisive. The value of γ comes out to be ∞ which would indicate that the function has no nodes in λ, a condition which is characteristic of the polar solution (2″). However, the more important criterion that β_n, β_e of like sign means polar type, of opposite sign means non-polar type, cannot be applied since β_n comes out to be zero. The values of the other parameters are $\alpha_n=1.5$, $\alpha_e=0.8$, $\beta_e=1.2$.

The most reliable empirical value of the electronic energy for the hydrogen molecule in the B-state is -31.10 volts, corresponding to a heat of dissociation of 3.37 volts.[15] With the above values of the parameters, the wave function (4) gives -30.15 volts.

An attempt was made to improve (4) by replacing $-\alpha_n\lambda_i$ by $-\alpha_n\lambda_i+\delta\mu_i^2$. The correct value of δ was found to be 0.62. The electronic energy was lowered to -30.37 volts, representing a heat of dissociation of 2.64 volts.

The authors wish to express their thanks to Professor E. C. Kemble for his ever helpful advice and criticism.

[15] Kemble and Zener, reference 2, p. 535.

ROTATIONAL INSTABILITY AND UNCOUPLING OF THE ELECTRONIC ORBITAL ANGULAR MOMENTUM FROM THE AXIS IN DIATOMIC MOLECULES

By William W. Watson*
Munich, Germany

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Abstract

A number of peculiar rotational phenomena exhibited by some molecular spectra are attributed to uncoupling of the electronic orbital angular momentum from the nuclear axis. The details of several diatomic hydride band systems are discussed as examples. This uncoupling would contribute to a condition of rotational ins ability, and is a factor in limiting the amount of rotational energy that these molecules can possess in these electronic states.

IN A previous paper[1] the descrepancy between the values of the heats of dissociation of some hydride molecules as reckoned from the vibrational energy data of their spectra and the values obtained from the apparently very definite maximum rotational energy displayed in the same electronic state by some of these molecules was pointed out. The possibility of explaining this rotational phenomenon in some instances as due to an uncoupling action on the electronic angular momentum vectors brought about by the nuclear rotation was suggested. It is the object of the present paper to discuss some examples of these rotational distortions in the light of this suggestion. O. Oldenberg has recently shown[2] by a graphical method, considering the law of the conservation of angular momentum for the rotating molecule, that the curves of energy as a function of r, the internuclear distance, display no minimum for values of the nuclear angular momentum greater than a certain definite amount. The molecule should be unstable for rotational states beyond this critical point, and its band spectrum should consequently show a sharp breaking-off of the branches at this rotational quantum number. There is no relation between this maximum rotational energy content, however, and the heat of dissociation as determined from the depth of the minimum of the potential energy curve $U(r)$ for the non-rotating molecule. But in addition to this general consideration, there is the possibility that in certain electronic states of the molecule a rather unstable condition will result from the effect of the nuclear rotational magnetic field with the consequent uncoupling of the electronic angular momentum from the internuclear axis.

The evidence for the existence of this uncoupling phenomenon for some of the electronic (singlet and unresolved triplet) levels of H_2 and He_2 spectra has been discussed by Weizel,[3] and for H_2 by Dieke.[4] Those rotational terms

* Fellow of the John Simon Guggenheim Memorial Foundation.

[1] W. W. Watson, Phys. Rev. **34**, 372 (1929).

[2] O. Oldenberg, Zeits. f. Physik **56**, 563 (1929).

[3] W. Weizel, Zeits. f. Physik **52**, 175 (1928); **55**, 483 (1929).
W. Weizel and E. Pestel, Zeits. f. Physik **56**, 197 (1929).

[4] G. H. Dieke, Zeits. f. Physik **55**, 447 (1929).

exhibiting anomalies in these spectra can be represented by the formula

$$F(j)=B\cdot[(j\cdot(j+1)-\Lambda^2)^{1/2}-\rho]^2+\cdots$$

in which Λ is the projection of the electronic orbital angular momentum l in the direction of the nuclear axis,[5] while ρ is the effective component of l perpendicular to this axis. For the lower rotational states, ρ is proportional to the nuclear rotational angular momentum, but has a limiting value l, of course, corresponding to complete uncoupling of l from the axis. It is found that the uncoupling is more marked the larger the principal quantum number of the excited electron, and the larger the value of l. The magnitude of the distortion produced by the uncoupling is indeed an indication of whether a p, d, etc., electron is involved, and thus is an aid in the interpretation of these complex spectra. If the uncoupling of the l from the internuclear axis is complete, the band lines should show a Zeeman effect independent[6] of j, whereas for the case of no uncoupling, the Zeeman splitting is proportional to $1/j^2$. Curtis and Jevons[7] have reported that all of the lines of the bands involving the z electronic state of He_2 show large Zeeman effects, and these particular bands show the largest uncoupling. It is to be especially noted that all the bands of the H_2 and He_2 spectra displaying the anomalies attributable to uncoupling have the sharp, sudden decrease in intensity of the branches at the highest j values.

In the determination of the character and energy of a molecular state, the quantity Λ is of prime importance, for according as Λ is 0, 1, 2, $\cdots$ the electronic level is designated as Σ, Π, Δ, $\cdots$. For example, in the formation of the AlH molecule, the lower $^1\Sigma$ state and the upper $^1\Pi$ state both probably come from the normal ^2P state of Al, the $3p$ electron becoming respectively a $3p\sigma$ electron and a $3p\pi$ electron in these two molecular states[8] which differ by 2.9 volts in energy. However, the rotational dissociation apparent in the $AlH\,{}^1\Pi\rightarrow{}^1\Sigma$ bands,[9] for the 0—0 band of which the branches break off sharply at $j=20$, is probably a consequence of the lack of a minimum in the potential energy curves[2] for $j>20$ in the upper state (the instability is not in the lower $^1\Sigma$ state, for these rotational terms can be followed to $j=28$ in the AlH $^1\Sigma\rightarrow{}^1\Sigma$ system), and is not due to an uncoupling action on the Λ, since the doubling in the $^1\Pi$ state is small, and there is no close-lying electronic state to create a resonance effect (see below).

The uncoupling of the electronic spin s from its interaction with Λ in the direction of the internuclear axis and its orientation with respect to the magnetic axis created by the nuclear rotation (transition from Hunds case (a) to case (b)) is well known (OH, MgH, etc., bands). But judging from the regular course of the rotational term values, there are no instances yet

[5] We use the band spectrum notation recently suggested: Λ is the same as the formerly used σ_A of Mulliken and i_l of Hund; K is used in place of Mullikens j_A to denote total angular momentum exclusive of the spin s.

[6] F. Hund, Zeits. f. Physik **36**, 673 (1926).

[7] W. E. Curtis and W. Jevons, Proc. Roy. Soc. **A120**, 110 (1928).

[8] R. S. Mulliken, Phys. Rev. **33**, 737 (1929).

[9] G. Eriksson and E. Hulthén, Zeits. f. Physik **34**, 775 (1925).
E. Bengttson, Zeits. f. Physik **51**, 889 (1928).

recorded among the spectra of molecules other than H_2 and He_2 of a strong uncoupling of l from the nuclear axis for the low rotational states. Such band systems, involving generally the more excited electronic states, and which should lie in many cases rather far in the ultra-violet, should present interesting anomalies. The existence of a doubling of the rotational levels when $\Lambda > 0$ (σ-type doubling)[10, 11] is evidence in itself, however, of a growing component of l along the rotation axis, and its gradual uncoupling from the internuclear axis. Large σ-type doubling, and the anomalous behaviour of the rotational terms that is attributable to uncoupling, are closely associated phenomena. Examples of this correlation are to be noted among the He_2 bands[12] and in the bands of CaH and BeH discussed below.

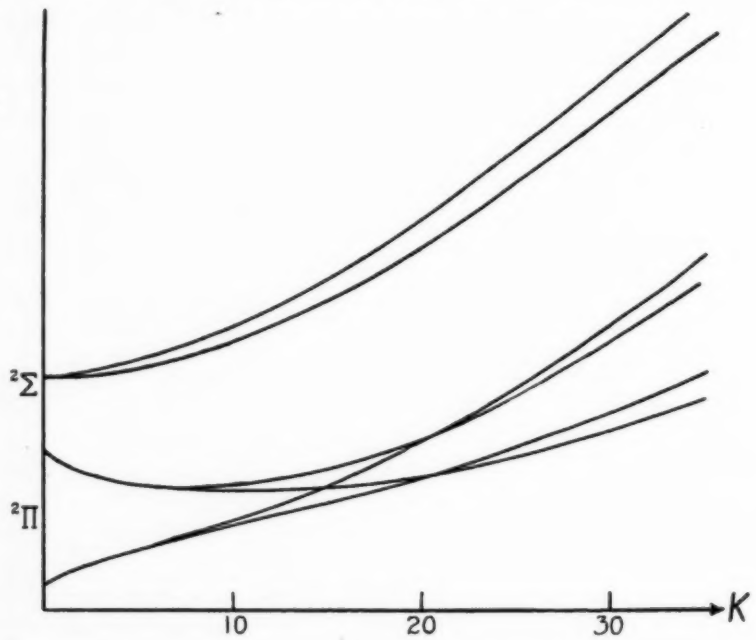

Fig. 1. Calcium hydride rotational terms. Separation of the $^2\Pi$ and $^2\Sigma$ levels much reduced as compared to scale used for splitting.

For the higher rotational states, however, the growing magnetic field of the rotation may exert a stronger influence on the orbital angular momentum than does the constant electric field in the direction of the nuclear axis. Hund[13] has given the splitting of the $^2\Pi$ and $^2\Sigma$ terms resulting from the ^2P state of the united atom for first, only the electric field present, then a a weak perpendicular magnetic field coupling the spin to its axis, and finally for the case where the magnetic field influences the l more than does the nuclear axis. Fig. 1 gives the course of the rotational levels for the $^2\Pi$ and neighboring $^2\Sigma$ (upper state of "B" bands) states of CaH. The data for the curves are

[10] J. H. Van Vleck, Phys. Rev. **33,** 467 (1929).
[11] R. de L. Kronig, Zeits. f. Physik **50,** 347 (1928).
[12] W. Weizel and E. Pestel, Zeits. f. Physik **56,** 197 (1929).
[13] F. Hund, Zeits. f. Physik **52,** 606 (1929).

taken from Hulthén,[14] the energies all being differences reckoned from that of the lowest $^2\Sigma$ state for the same rotational level, and with the separation of the electronic states much reduced. The marked similarity with Hund's curves is apparent. Noteworthy are the very large σ-type doubling[15] and crossing of the components at $K=20$ in the $^2\Pi$ state, the unusually large doubling in the Σ state,[15] and the tendency of the curves in the two states to bend toward each other at their extremity. There is also a rather sharp decrease in the intensity of the series in these bands for the highest K values, particularly in the vibration level (1) of the $^2\Sigma$ state.[14] Now the likely configuration[16] for the outer electrons in this $^2\Sigma$ state in CaH is $4s\sigma^2 3d\sigma$, which makes the chance for uncoupling good[17] ($l=2$, $\Lambda=0$). Since the doubling in each σ-type doublet component for $K>20$ is proportional to K, as in "ρ-type" doubling,[10] it must owe its origin to an effective component of l in the direction of the rotation axis.

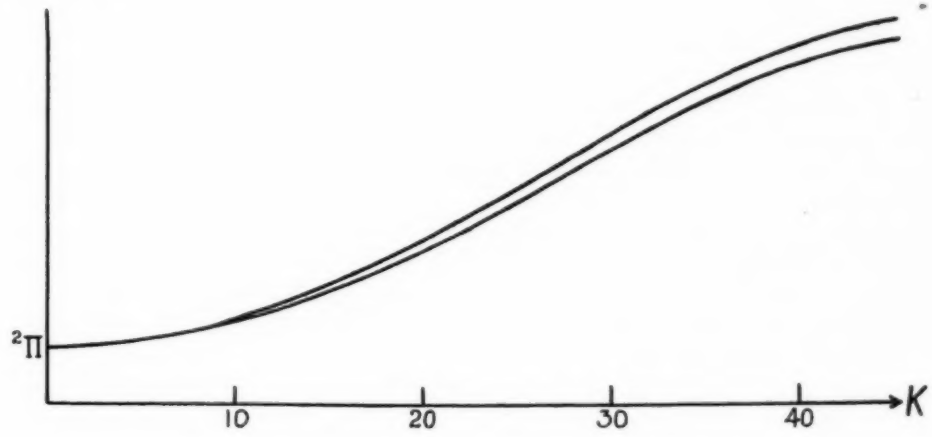

Fig. 2. Beryllium hydride rotational terms for $^2\Pi$ level.

The green BeH bands[18] also exhibit a marked reverse bending of the branches for the higher rotational levels. Fig. 2 represents the course of the rotational levels in the upper electronic state, which is probably $2s\sigma^2 2p\pi\ ^2\Pi$ and strong case (b). An exceptionally large rotational energy of over 2 volts

[14] E. Hulthén, Phys. Rev. **29**, 97 (1927).

[15] There is a little doubt as to the exact numbering of the Q branches, and hence as to the exact magnitude of the doublet width. However, any slight error in the assignment can not vitiate our conclusions, for the doubling is certainly very large in both the $^2\pi_{1/2}$ and $^2\pi_{1\ 1/2}$ components. Van Vleck[10] has suggested that a close resonance between these neighboring Σ and Π states may be responsible for this anomaly, as well as for the large doubling in the $^2\Sigma$ state, in view of his explanation of the doubling in Σ states as a rotational distortion effect, taking into account the component of orbital angular momentum perpendicular to the nuclear axis.

[16] R. S. Mulliken, Phys. Rev. **33**, 730 (1929).

[17] The sharp breaking-off of the series in the C band of CaH is probably due to a very low heat of dissociation in the upper $4s\sigma^2 5s\sigma^2\Sigma$ level, and represents an instability such as Oldenberg considers.

[18] W. W. Watson, Phys. Rev. **32**, 600 (1928).

at $K=45$ is here attained. To be noted are the large σ-type doubling and the shift of the levels to lower energy for the higher K values. The doubling is apparently exactly equal in the two coinciding spin components, and follows a different law from $K=35$ to the end, the doublet width in the last stretch being almost constant. Now Van Vleck's general energy formula[19] for the $^2\Pi$ state includes terms which are corrections for the influence of the Σ states, and "whose most interesting effect is the introduction of σ-type doubling." Apparently also these terms predict just such a bending of the branches as is here observed, however, if the component of l perpendicular to the nuclear axis is appreciable. Assuming that l is completely coupled to this perpendicular axis (uncoupled from the internuclear axis), approximate calculation shows that the shift of the rotational energy curve for the highest K value should be about that found experimentally.

Recently Pearse[20] has analysed an ultra-violet MgH band system which is the second member of the $^2\Pi \rightarrow {}^2\Sigma$ MgH series with the configuration $3s\sigma^2 4p\pi$ as against $3s\sigma^2 3p\pi$ for the green bands.[16] This is particularly interesting for our present discussion, because it forms the only example yet known for a molecule other than H_2 and He_2 for which the effect of the increase in the size only of the electron orbit can be studied. As in the case of the H_2 and He_2 bands, the increase in the principal quantum number increases the uncoupling effect on the Λ component of l, judging from the markedly increased σ-type doubling. Also there is a sharp cut-off of the R and P branches for lines corresponding to the same initial level, $K'=10$. The Q branch shows no such sharp break, however, but is well developed to beyond $K=23$. Apparently the sudden drop in intensity in the R and P branches is so definite that it cannot be merely a question of the relative intensity of the R and P as against the Q transitions. Since the explanation could not be the lack of a minimum in the potential energy curves, it is quite probably the result of an uncoupling of the orbital angular momentum from the nuclear axis. With complete uncoupling there is no further σ-type doubling in the Π state, and succeeding rotational transitions must be either only P, R-type or only Q-type. Since the latter transitions persist, it would appear as if such a rotational distortion phenomenon could invoke the forbidden $0 \rightleftarrows 0'$ transition[21] for Λ, although of course this is not to be considered as a real $\Sigma \rightleftarrows \Sigma'$ transition.

From this brief discussion of the anomalous course of the rotational energy in a few band systems, it is to be concluded that the uncoupling action on the electronic angular momentum in the higher rotational states is of rather frequent occurrence, and is a factor to be reckoned with in considering the rotational stability of molecules. A quantitative treatment of the uncoupling processes, and further exerimental investigation of higher molecular electronic states and of the Zeeman effect for high rotational levels, should yield interesting information on these points.

[19] Ref. 10, Eq. 61, p. 497.
[20] R. W. B. Pearse, Proc. Roy. Soc. **A122**, 442 (1929).
[21] E. Wigner and E. E. Witmer, Zeits. f. Physik **51**, 859 (1928).

THE REFLECTION OF THE $K\alpha$ LINE OF CARBON FROM GLASS

By Elmer Dershem
Ryerson Physical Laboratory, University of Chicago.

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Abstract

A vacuum spectrograph was constructed in which a beam of monochromatic radiation in the extremely soft x-ray region could be isolated by means of a ruled grating and then reflected from a mirror. This mirror could be rotated and the intensities of the reflected rays corresponding to various glancing angles of incidence could be compared by a photographic method. Using a glass surface and the $K\alpha$ line of carbon (wave-length = 44.6A) measurements of reflected intensity were made for glancing angles of incidence between 1° and 8°. At 8° the reflected intensity was found to be less than 4 percent of the intensity at 1°. However the curve relating intensity of reflection with glancing angle of incidence shows no abrupt change of slope, such as would occur in the case of hard x-rays. This indicates that absorption effects modify the intensity of the reflected ray sufficiently to obscure any sudden change at the critical angle in the case of the reflection from glass of wave-lengths as long or longer than 44.6A.

THIBAUD[1] has endeavored to measure the critical angle of total reflection from a glass surface by varying the angle of incidence of a beam of x-rays upon a glass grating and determining the angle, for each line in the spectrum, at which the intensity of that line had decreased to one-half value and also the angle at which it had entirely disappeared. For the $K\alpha$ line of carbon he found the angle at which the intensity had decreased to one-half value to be 5×10^{-2} and the angle for complete disappearance to be 5.1×10^{-2}. Expressed in degrees and minutes these angles are 2° 52′ and 2° 56′ respectively. This indicates a rapid decrease in reflected intensity between these angles and would seem to locate the critical glancing angle of total reflection with some definiteness. However, at another place in the same article he gives the angle for complete disappearance of the carbon line as 6.4×10^{-2} which is 3° 40′. Also no statement is made concerning the angle at which 100 percent intensity was obtained for the carbon line.

Henderson and Laird[2] have sought to determine critical angles by measuring the intensity of the reflected radiation when soft x-rays, generated at constant voltage, were caused to fall at various glancing angles of incidence upon glass and iron surfaces. Their curves for a glass surface show that with 194 volts applied to the x-ray tube, the intensity of reflected radiation falls quite uniformly as the glancing angle of incidence is increased from 1° to 20°. The intensity at the larger angle being about 26 percent of that at the smaller. A nearly parallel curve was obtained with 576 volts. In the latter case the intensity of reflected radiation at 20° was about 22 percent of that at

[1] Thibaud, Comptes rendus **187,** 219 (1928).
[2] Henderson and Laird, Proc. Nat. Acad. Sci. **14,** 773 (1928).

1°. Since the quantum voltage corresponding to the $K\alpha$ line of carbon is about 275 volts the curve relating intensity of reflection of this line with angle of incidence should lie somewhere between the above curves provided that this method is really applicable to the problem. Since an increase in tube voltage merely shifts the position of maximum intensity of radiation toward shorter wave-lengths without eliminating the longer wave-lengths upon which the maximum angle of reflection depends, it appears doubtful that any definite information concerning critical angles of reflection may be thus obtained.

Since neither of these methods makes a direct attack upon the problem a vacuum spectrograph was designed and constructed in which measurements of reflected intensity could be made with the use of strictly monochromatic lines obtained from a ruled grating. The $K\alpha$ line of carbon is one of the most prominent and intense lines in this region and hence was chosen first for investigation.

Apparatus

The arrangement of the principal parts of the apparatus used in this work is shown in Fig. 1. The spectrograph, mounted upon a steel frame extending upward from the brass base plate B, could be enclosed for evacuation by the brass cylinder C which rested upon the rubber gasket E. This cylinder could be raised by means of a cord and pulley, thus conveniently exposing the apparatus for adjustment and for the changing of photographic plates. The x-ray tube, partly shown at X, has been previously described.[3] The x-ray beam passed upward through two rather wide slits before entering the spectrograph chamber. These somewhat reduced the intensity of the light from the filament. The beam then passed through the collimating slits S_1 and S_2 which were 0.25 mm wide. The plane glass grating G, having 600 lines per mm, was set at an angle of 4° 41′ with respect to this beam. This produced an intense first "inside order" of the $K\alpha$ line of carbon, deviated 6° 43′ from the direction of the incident beam. The arm A carrying the mirror M and the slit S_3 could be turned about an axis passing through the line of incidence of the x-ray beam upon the grating. By taking suitable photographs of the carbon spectrum it was possible to find the angular setting for the arm A which would permit only the central portion of the $K\alpha$ line to pass through the slit S_3 and fall upon the mirror M. The ratchet R could be turned by means of an electromagnet (not shown in the drawing) and the angle of the mirror changed by small known increments from outside the apparatus. The shield and slot S_4 could be caused to move across the path of the reflected beam by means of an electromagnet, likewise controlled from outside. Hence its position could be adjusted so that all parts of the photographic plate were shielded from stray radiation except the part which was being exposed to the beam reflected from the mirror. Another electromagnet gave a step by step translational motion to the photographic plate. Each time the angle of the mirror was changed the shield was moved by such an amount

[3] Dershem, J.O.S.A. & R.S.I. **18**, 127 (1929).

that the reflected ray would pass through the slit and the photographic plate was moved so that a fresh portion of the plate was exposed. In this way a series of lines could be obtained upon the plate, each being due to the same wave-length but reflected at different angles from the mirror.

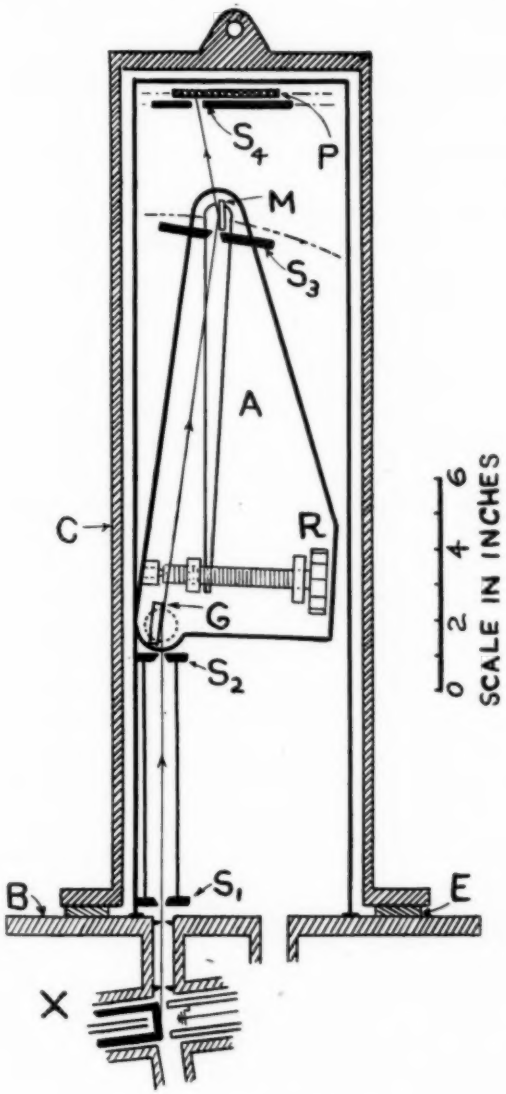

Fig. 1. Sketch of apparatus.

One three stage mercury pump was used to evacuate the spectrograph chamber and another to evacuate the x-ray tube. The pressure in the apparatus ranged between 10^{-4} and 10^{-5} mm Hg. The x-ray tube target was a tungsten button embedded in copper. However the carbon line, due to stopcock grease, always appears. It is possible, by the use of large energy input,

to burn off most of the carbon deposited on the target and thus reduce the intensity of the carbon line. In this work 50 ma and 4.2 kv, rms were used and with this power input the intensity of the carbon line usually remained constant but sometimes increased in intensity at a rate of about 5 percent per hr.

For most of the observations taken in this work the mirror was first set at a glancing angle of 2° and an exposure of three or four minutes duration was made. The mirror was then advanced in steps of 15′ each and the time of exposure increased with increase of angle, each exposure being made on a fresh portion of the photographic plate. After several exposures had been made upon a plate, each for a different angle of incidence upon the mirror, the latter was caused to return to the original angle of 2° by means of another electromagnet, also not shown in the drawing. A check exposure was then made upon the photographic plate to determine whether, or not, the intensity of emission of the carbon line had changed since the first exposure. In order that the mirror might intercept the entire beam passing through the slit S_3 the latter was made narrower for angles less than 2° than was desirable at larger angles. However in every case the ray reflected at an angle of 2° was recorded at least once upon each plate. Hence the intensities at all angles could be compared with the intensity at 2° as recorded upon the same plate under as nearly the same conditions as it was possible to obtain.

Results

Eastman x-ray plates were used in this work and it was found that useful comparisons of the densities of lines on these plates could not be obtained with either the Moll or the Hartmann microphotometers. This was partly due to the rather low density of blackening that could be obtained at large angles of reflection in a reasonable time of exposure. Hence recourse was had to a method of direct visual comparison with lines of varying density upon another plate. Such a comparison plate was obtained by keeping the angle of reflection constant while the photographic plate was advanced in steps of 4 mm each. At each step the time of exposure was gradually increased and a series of lines of uniformly increasing density of blackening was thus secured. A number of comparison plates were made in a similar way with the use of other time intervals of exposure.

The relationship between intensity of blackening and time of exposure is not precisely known in this wave-length region and cannot easily be measured. Hence the reciprocity law of blackening is assumed in what follows. Presumably the errors due to the assumption of this law are less than the probable errors of observation.

Assuming the validity of the reciprocity law, it follows that the ratio of the intensities of the rays reflected at two different angles is equal to the product of the ratio of the densities of blackening and the inverse ratio of the times of exposure. The ratio of blackening was obtained in the following way. The photographic plate was placed with its film side in contact with the film side of one of the comparison plates described above. Each line of

the plate under test was matched with a line of the comparison plate, estimated interpolations being made in the case of intermediate densities. Since the intensity of radiation was constant for all lines of the comparison plate the ratio of blackening of any pair of lines on the plate under test was given directly by the ratio of the times of exposure of the corresponding lines of the comparison plate.

In this way the intensity of the radiation reflected at each angle was independently compared with that reflected at 2° as recorded upon the same plate. In a similar manner intensity comparisons for the same angles were secured from other plates. In each case estimates were made with the use of several comparison plates. As previously stated a different width of slit was used for angles between 1° and 2°. Hence a different series of plates

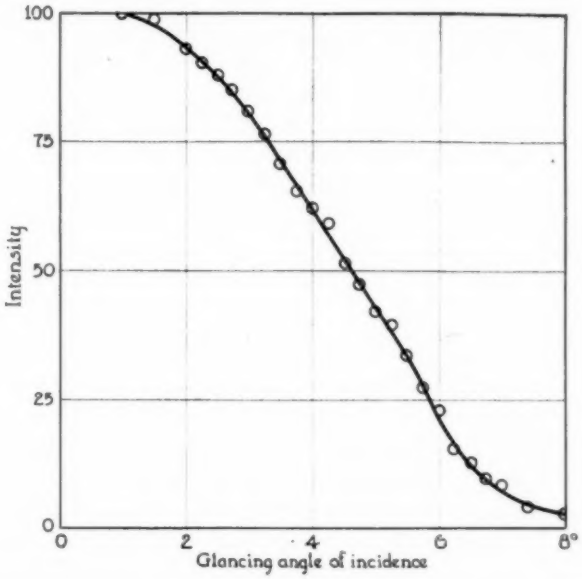

Fig. 2. Intensity of reflection of the $K\alpha$ line of carbon from glass for various glancing angles of incide ce

was used to determine the ratio of the intensities at these angles. With this ratio known the intensity at all angles could be compared with that at 1°.

The values thus obtained for the intensity of reflected radiation at a given angle were then averaged and the results are shown in Fig. 2. The accuracy of the method may be judged somewhat by the probable error of observation. For example, the intensity of the radiation reflected at 4° compared to the intensity at 1° was found from 24 observations to be 62.3 ± 0.8 percent. The results of the same number of observations at 5° and 6° was 42.2 ± 0.9 and 23.0 ± 0.4 percent respectively. These computations and similar ones for other angles indicate that the average probable error of observation was not greater than 2 percent. This conclusion is also borne out by the close approach of all the points to a smooth curve. In obtaining these results no estimates were discarded.

The curve of Fig. 2 shows no sudden change of slope which might be taken to indicate the value of the critical glancing angle of total reflection. In this respect it does not confirm the results of Thibaud,[1] the decrease in reflected intensity being much more gradual with increase of angle than indicated by his work. Also the reflected ray is shown to persist with relatively large intensity far beyond the limiting angle which he found. On the other hand these results show that the decrease in reflected intensity with increase of angle is much more rapid than would be inferred on the assumption that the results of Henderson and Laird[2] were really related to this problem.

The sudden change in reflected intensity which occurs at the critical angle in the case of a transparent medium becomes less abrupt in the case of an absorbing one. This effect has been discussed by Prinz.[4] If the coefficient of absorption is sufficiently large the variation in reflected intensity with angle of incidence becomes fairly uniform in the neighborhood of the critical angle with result that the latter may not be definitely located by the presence of any discontinuity in the curve. The results obtained in the present investigation may be explained by such considerations as these. It appears evident that in the case of glass and radiation having a wave-length as long as 44.6A that the coefficient of absorption is sufficiently large to obscure the angle of critical reflection quite completely.

If the index of refraction were known the critical angle could be found by computation. Thibaud[1] has endeavored to do this for the case of the $K\alpha$ line of carbon reflected from glass. He determined the index of refraction by the use of the simplified form of the Drude-Lorentz dispersion formula which is known to give fairly accurate results provided that the frequency of the radiation is much higher than any critical frequency of the elements composing the reflecting substance. In this way he obtained a theoretical value of $6° 40'$ for the critical angle. It is doubtful that any serious importance may be attached to such computations in this region since the frequency of the $K\alpha$ line is lower than some of the critical frequencies of the principal constituents of glass. The effect of these critical frequencies is to diminish the critical glancing angle. Hence the true value is certainly less than that computed as above. This is borne out by an inspection of the curve of Fig. 2 which shows that the reflected intensity has fallen to a very low value at the above angle.

It is planned to extend this investigation with the use of other wave-lengths and other reflecting surfaces. In conclusion I wish to extend my thanks to Professor A. H. Compton and the Ryerson Laboratory Staff for placing the facilities of the laboratory at my disposal for this investigation and for many helpful suggestions during the course of the work. I wish also gratefully to acknowledge the loan by the Department of Physics of the University of California of the x-ray tube used in this investigation.

[4] Prinz, Zeits. f. Physik **47**, 479 (1928).

THE REFLECTION OF X-RAYS FROM PLATINUM FILMS SPUTTERED ON GLASS

By H. E. Stauss
Brace Laboratory of Physics, University of Nebraska

(Received August 15, 1929)

Abstract

The reflection of x-rays from films of platinum of varying thicknesses sputtered on glass was studied to determine if there was a variation of the critical angle of reflection with the thickness of the film, such as is observed in the case of nickel. Although some difficulty was met in determining the critical angles, the results indicate that there is a similar variation of the maximum angle of reflection. The critical angles of several silver films, sputtered under as nearly identical conditions as possible, were found to differ by amounts much greater than can be attributed to experimental errors. No effort was made to determine if there was a variation with thickness. In the cases of a number of films strong scattered radiation having deviations as great as 1°46′ with the primary beam was observed. The reflected beam proper formed the lower limit of the scattered beam. As heterogeneous radiation was being used, it could not be determined whether the reflected wave-lengths were also being scattered.

IN A previous investigation[1] it was discovered that the critical angle of reflection of x-rays for nickel films sputtered on glass increased with the thickness of the films. This was systematically investigated by Edwards,[2] who found that the relation held for all thicknesses so long as the film was not too thick. It seemed worth while to determine if the phenomenon was present in some other metal sputtered on glass. Platinum was chosen because it might be expected to be free from chemical reactions that would contaminate the surface. The results are not as satisfactory as could be desired, but are being reported now because the author will not be in this laboratory next year.

The arrangement of the apparatus was similar to that described by Edwards.[3] It differed in that the distance from the slit near the x-ray tube to the mirror was equal to that from mirror to photographic film. It can be shown that for this arrangement the error made in measuring the critical angle of reflection on account of the divergence of the incident beam lies between zero and twice the angle subtended by the first slit at the mirror. For the slit near the tube the one described previously[4] was used. Its effective width was less than 0.013 mm. The distance from slit to mirror was 125 cm. Consequently the error due to divergence of the beam was less than 5″.

[1] H. E. Stauss, Phys. Rev. **31,** 491 (1928).
[2] Hiram W. Edwards, Phys. Rev. **32,** 712 (1928).
[3] Hiram W. Edwards, Phys. Rev. **30,** 91 (1927).
[4] H. E. Stauss, J.O.S.A. and R.S.I. **17,** 365 (1928).

The experimental procedure was a modification of Edwards.[3] The general radiation from molybdenum was used, and the critical angle of reflection of the $K\alpha$ radiation was located by the sharp change in the intensity of reflection at this point. Since the primary purpose of the investigation was the study of the dependence of the critical angle upon the thickness of the film, sufficient accuracy could be attained by reflecting the radiation at discrete positions of the mirror (positions usually separated by 30″) and by assuming the critical angle to lie between the last reflecting position and the first non-reflecting one. For the platinum films no really sharp change in intensity of reflection was observed. In this respect it was unlike the glass back or silver films. A position could be located at which there was a change in intensity, but fairly strong reflection which gradually weakened continued beyond this angle. The films were sputtered in a dessicator jar with a grease seal above the electrodes. The first ones were sputtered at a very slow rate and were clean and clear. Thicker ones, which were not used, however, were discolored. Later the apparatus was changed slightly to permit more rapid sputtering, and thicker, clear films were then obtained. The later films were protected during sputtering by a crystallizing dish inverted over the platinum electrode and the mirror; but tests by Mr. Koontz of this laboratory showed that the effect of the grease seal was negligible. The chief cause of the discoloration of sputtered silver films lay in the silver electrode itself. The films were sputtered from a platinum dish onto a single glass back—a thicker one being obtained by an added deposit on the previous thinner film. It was observed that the films, if allowed to stand in concentrated nitric acid or sodium hydroxide, flaked loose, even though they did not react chemically.

The following table shows the results obtained. The time of sputtering is given in each case, but since so many factors affect the rate of deposition, nothing certain can be stated about the relative thicknesses of the films. On account of the uncertainty of the determination of the critical angle, two values are given,—one determined from the position of the change in intensity of reflection which might be interpreted as the critical angle, and the other from the last angle at which reflection was observed. On the whole there is a definite trend towards increasing angles of reflection with increasing thickness of film. The angles are listed with the possible, or maximum, relative errors; i.e., the errors in the distance from mirror to film, which would introduce an additional error of about 3″, are neglected.

Films sputtered for 40 and 55 minutes did not differ appreciably in their critical angles and behaviour from the one sputtered for 25 minutes. All the films were transparent, but the last was opaque to all except the strongest sources. Four attempts were made to sputter opaque films. The first, sputtered by the slower method, was discolored. Two sputtered by the faster method were clean, but they had very low optical reflectivity. They can be best described as approaching the condition of platinum black. The

reflection from one was tried, surface 7 in the table, and was found to be very poor and to stop at a very small angle. A third film was discolored.

Surface	Critical angle corresponding to change in intensity	Critical angle corresponding to last angle of reflection	Description of surface and comments
Glass	5′58″ ± 5″		Critical angle determined by Edwards' method
"	5′56″ ± 20″		Critical angle determined by discrete positions after the second film of platinum had stood over night in aqua regia.
Platinum (1)	6′57″ ± 35″	7′57″ ± 35″	A very thin, practically invisible film sputtered for 15 min.
" (2)	6′13″ ± 20″	6′43″ ± 20″	The surface after the previous film had been washed off.
(3)	6′ 9″ ± 20″	6′39″ ± 20″	A very thin film sputtered for 30 min. after the preceding one had stood overnight in aqua regia.
" (4)	6′55″ ± 20″	7′25″ ± 20″	Sputtered for 1 hour.
" (5)	7′45″ ± 35″	9′45″ ± 35″	Sputtered for 1½ hours.
" (6)	11′35″ ± 35″	12′36″ ± 35″	Sputtered for 25 min. after the apparatus was modified.
" (7)		6′42″ ± 35″	Nearly opaque film sputtered onto #6.

Several details may be noted. The second film listed under platinum was really the glass surface from which the previous film had been washed with aqua regia. The last angle of reflection is definitely greater than that for glass. Apparently the platinum had penetrated into the glass and was not readily reached by an ordinary washing. Soaking the glass over night caused the critical angle to return to the value for glass. The last, nearly opaque film had a lower critical angle than the thinner base film, probably on account of the roughness of the surface. This raises the question as to what extent surface conditions affect the reflection of x-rays.

The cause of the fading at the critical angle is uncertain. Irregularities in the density of the film might have produced it. These may have been due to irregular mixing of grease with the film in sputtering; to a possible irregular deposition of the constituent metals if the dish should have been made of a platinum alloy, or to an irregular thickness, if the thickness affects the density. The use of heterogeneous radiation, with its varying distribution of intensity among the wave-lengths, may have caused it in some way. There is also the possibility that the surface conditions produced the fading. However, whatever the cause of the fading, the results indicate that the maximum angle of reflection of the films increased with the thickness of the films.

In order to test the sharpness of the critical angle in another metal, a study was made of the reflection from silver films. No effort was made to find a variation with thickness, but the results showed that there may be a variation in the critical angles of films produced under as nearly identical

conditions as possible.[5] The films were all sputtered for 12 minutes under the same conditions and were all transparent. The critical angle of reflection was comparatively sharp in all cases. Four values of the critical angle were obtained, $11'7''\pm20''$, $11'25''\pm2''$, $11'0''\pm2''$, $11'45''\pm2''$. The first film was studied by the method of discrete positions; the others by Edwards' method. The errors given for the last three are the probable errors of the measurements of the photographic films expressed in angles, or the relative probable errors. The second and third determinations were made from the same film, the measurements being made one week apart. The last film, although transparent, gave a result in close agreement with the theoretical value for the critical angle.

On a number of films refracted radiation was observed. It has been shown[6] that the deviation produced by a prism, when the angle of incidence is near the critical angle of reflection, is very insensitive to changes in the prism angle. Consequently it was expected that the refracted radiation might give a clue to the true index of refraction of the films. Because of the relation between the deviation and the angle of incidence that holds for x-rays, the observed refracted radiation must have been limited by the $K\beta$ wave-length. The angles of deviation for glass and silver were $4'0''$ and $4'58''$. The values of δ, one minus the index of refraction, calculated from the deviation of the refracted beams, if they are converted to the value for the $K\alpha$ radiation, are 1.46×10^{-6} and 4.59×10^{-6}, respectively, as compared with the values 1.51×10^{-6} and 5.85×10^{-6} determined from the critical angles of reflection from the same surfaces. The refracting angle was asumed to be 90° in each case. The great discrepancy in the case of silver can hardly be considered a real difference in the index of refraction as determined by the two methods. The discrepancy cannot be attributed to errors in the prism angle, because the angle which would have produced the observed deviation, if the value of δ is that obtained by reflection, is less than 1°. Such a value is impossible. It is probable that both the silver and the glass took part in the refraction. Consequently refraction could not be used as a check on the reflection.

In the course of this work an observation was made which seems not to have been reported before. On five different photographic films, corresponding to five sputtered films, four of platinum and one of nickel, the reflected beam was the limit of a much weaker beam. Angles of deviation from the primary beam as much as $1°6'$ to $1°46'$ (about 1° to $1°30'$ with the mirror) were measured. These values were not the limit of the radiation, but the limit to which it could be observed on account of the film-holder. The exposures were from 15 to 40 minutes on duplitized film. Since heterogeneous radiation was being used, it could not be determined whether the reflected wave-lengths were also being scattered.

[5] These results are in accord with those reported by Dershem in the field of soft x-rays. Phys. Rev. **33**, 659 (1929).

[6] H. E. Stauss, J.O.S.A. and R.S.I. in print.

Two suggestions have been made to explain the variation of the critical angle with the thickness of the film in the case of nickel—that the densities of the films vary,[1] and that the critical angle is affected by the back supporting the film (the density of the films remaining unchanged) and that the extent of the influence depends upon the thickness of the film.[2] The results reported here indicate that the variation of the maximum angle of reflection with the thickness of the film is not peculiar to nickel, but they do not help to explain the cause of the variation.[7]

[7] In this connection it is desirable to point out that while the back may influence the reflection, this can hardly be through penetration of any great amount below the reflecting surface by the reflected beam or any considerable part of it. The penetration can be expected to introduce differences of phase into the reflected beam, and thus to weaken it considerably or to destroy it entirely. In his latest paper, Phys. Rev. 33, 463 (1929) Edwards feels that he has established that penetration into the back by the reflected radiation does occur. However, he cannot be sure that he was always observing the reflection from the nickel, unless he assumes the result that he desires to prove. If the penetration is assumed small, then when the nickel ceases reflecting, the radiation passes through it, but is reflected in turn by the platinum (if the nickel film is assumed to have plane parallel faces). Thus the observed critical angle is that of the platinum-nickel interface and not that of the nickel surface. However, as the nickel film becomes thicker, it absorbs more of the radiation passing through it and the reflection from the platinum becomes negligible. For nickel on platinum, one would expect the observed critical angle to be that of platinum for the thinnest nickel films, and to be that of nickel for the thicker ones. Edwards' results do not permit of a clear-cut choice between this possibility and the one which he suggests.

TOTAL RADIATION FROM POLISHED AND FROM SOOT-COVERED NICKEL

By B. T. Barnes
Lamp Development Laboratory, General Electric Co.

(Received August 23, 1929)

Abstract

Total radiation data were obtained on polished nickel and on the same metal when covered with soot. Temperatures below the range of an optical pyrometer were determined from a log-resistance vs log-temperature curve obtained from resistance measurements on the wire mounted in a lamp in a furnace at known temperatures and extended up to the points obtained when using a pyrometer. The log-resistance vs log-temperature curve had a sharp break at the magnetic transformation point just as noted by previous investigators. This break occurred at about 360°C. In the region from 800 to 900° the total radiation values for unpolished nickel deviated somewhat from a smooth curve through the values at lower and higher temperatures. This may be due to an error in drawing the log-resistance vs log-temperature curve since there were no resistance temperature measurements from 500 to 725°C between the range of the furnace readings and that of the pyrometer. Total emissivity values for soot-covered nickel range from 0.92 at 400°K to a mimimum value of 0.81 at 800°K, then rise to 0.86 at 1100°K. The total emissivity of polished nickel was found to be 0.205 at 1400°K. At 400°K it was 0.087 before heating to incandescence and 0.063 afterwards. At intermediate temperatures there were similar differences due to surface changes during the initial heating.

DATA on the total amount of energy radiated from substances as a function of the temperature are rather meagre. In the case of nickel total radiation values from 463 to 1181°K have been published by Suydam.[1] The curve he obtained on plotting his results changed slope near the magnetic transformation point just as the resistance-temperature curve does. A curve given by Kahanowicz[2] for the total emissivity between 540 and 800°K has a break at this point. His values for the total emissivity are in fair agreement below 650°K with those computed from Suydam's data, but between 650 and 800°K are as much as 60 percent higher. Suydam's values were obtained by a method ordinarily regarded as more reliable than the one used by Kahanowicz.

Total radiation data for soot-covered surfaces seem to be lacking except for measurements on the variation of the emissivity with the thickness of the coating for a temperature of 100°C by Kurlbaum[3] and for 184°C by Ruben and Hoffman.[4]

[1] Suydam, Phys. Rev. **5**, 497 (1915).
[2] Kahanowicz, Rend. Accad. Linc. **30**, 136 (1921).
[3] Kurlbaum, Ann. d. Physik **67**, 846 (1899).
[4] Rubens and Hoffman, Preuss. Akad. Wiss. Ber. **27**, 424 (1922).

Apparatus and Method

The present investigation employed a method for determining temperatures below 1000°K somewhat similar to that used by Suydam[1] and extended measurements to higher temperatures by use of an optical pyrometer. About 60 cm of the wire in the case of polished nickel or 30 cm of the soot covered metal was bent into a hairpin filament and mounted in a tubular lamp. The filaments had leads fused on each side of the tip so that the potential drop across 10 to 15 cm of the uniformly heated filaments could be measured. This lamp was connected to a mercury diffusion pump backed by an oil pump during both resistance and radiation measurements. For temperature-resistance measurements from room temperature up to 500°C the lamp was surrounded by a furnace consisting of an iron tube wound with nichrome wire. The temperature of the furnace was measured by a thermocouple located opposite the tip of the filament. In measuring the resistance a current so small that it would heat the wire less than 1° was used. Filament temperatures of 1000°K and above were measured by direct observation with an optical pyrometer. For polished nickel the corrections for obtaining true temperatures from brightness temperatures were computed by using the value 0.375 given by Worthing[5] for the spectral emissivity at wavelength 0.665μ. For soot-covered nickel the relation between true temperature and brightness temperature values was obtained from optical pyrometer readings[6] on special tubular filaments which had been covered with a layer of carbon similar to that deposited on the wire used for total radiation measurements. Viewing the black body cavity inside the hollow filament through small holes gave the true temperature and viewing the surface gave the brightness temperature.

For total emissivity measurements filaments 10 mils in diameter were used and approximately the same procedure followed in the case of both sooty and polished nickel. After evacuating a lamp the furnace was put on and resistance-temperature data from room temperature to 500°C were obtained. Then the filament was heated electrically to temperatures ranging from 400°K to incandescence and the current and voltage measured. Pyrometer readings were also taken as soon as the filament became bright enough, i.e., starting at about 1000°K. After reaching the maximum temperature desired the current was decreased in steps until 400°K was reached, the pyrometer, voltage and current readings being taken on the way down also. Then another temperature-resistance test was taken with the lamp in the furnace. Log-resistance vs log-temperature curves were drawn using both furnace and pyrometer data. All temperatures below the range of the pyrometer were obtained from this curve.

Experimental Data

A typical log-resistance vs log-temperature curve is given in Fig. 1. It resembles curves given by Suydam[1] and by Angell.[7] The points obtained on

[5] Worthing, Phys. Rev. **28**, 184 (1926).
[6] Pirani, Phys. Zeits. **13**, 754 (1912).
[7] Angell, Phys. Rev. **33**, 428 (1911).

first heating up the furnace lay on the same curve as those obtained on cooling, and the curves obtained before and after heating the filament to the maximum temperature (about 1100°K for sooty and 1400°K for polished nickel) were nearly identical in most cases. The break in the curve indicating the magnetic transformation point usually was at about 360°C.

The average of true-temperature minus brightness-temperature values on three tubular filaments covered with a layer of soot ranged from 5° at 1025°K to 8° at 1200°K. Because of non-uniform filament temperature these data are not as accurate as could be desired but are quite satisfactory

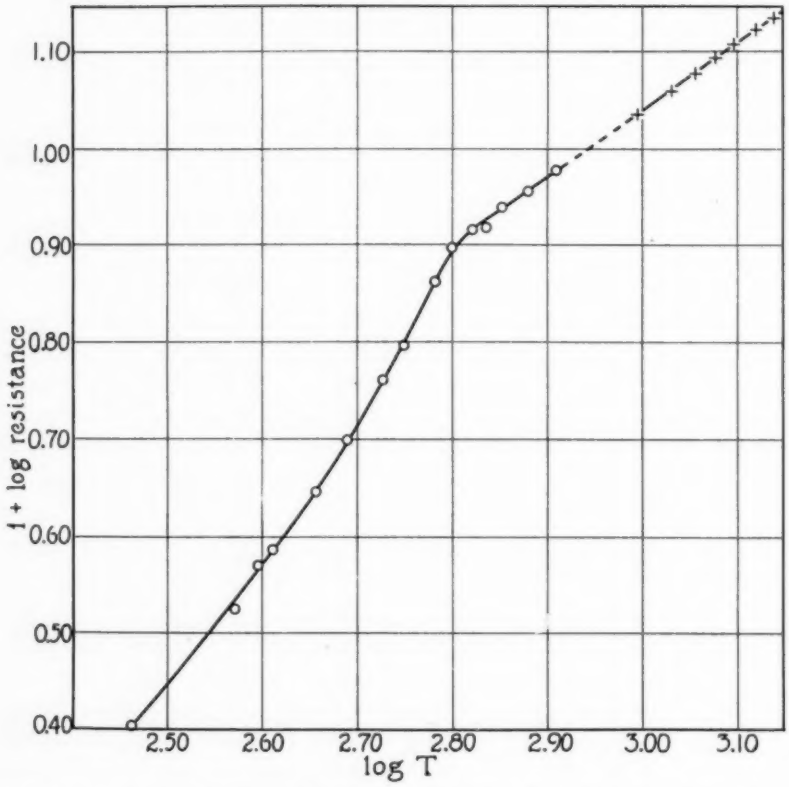

Fig. 1. Log-resistance vs. log-temperature curve for a 10 mil nickel wire. Distance between potential leads 12.8 cm.

for the present investigation. Averages of total radiation values with the surroundings at about 20°C obtained on three polished nickel filaments and on two soot-coated ones are given in Table I.

The corresponding emissivity curves are given in Fig. 2 with the value computed from each observation plotted. Curve *A* shows the results for soot-covered nickel, curve *B* for polished nickel on first heating and curve *C* for the same samples after the measurements had been continued up to a temperature of 1400°K. The solid circles in the neighborhood of curve *B* give emissivity values computed from Suydam's data on polished nickel.

TABLE I. *Total radiation (watts per cm²)*

Absolute temperature(°K)	*400*	*500*	*600*	*700*	*800*	*900*	*1000*	*1100*	*1200*	*1300*	*1400*
Soot-coated nickel	0.096	0.28	0.59	1.09	1.87	3.0	4.8	7.2			
Polished nickel, initial heating	0.0092	0.032	0.079	0.166	0.31	0.55	0.91	1.44	2.17	3.17	4.49
Polished nickel after reaching max.temp.	0.0066	0.023	0.058	0.123	0.24	0.44	0.76	1.28	2.04	3.09	4.49

DISCUSSION OF RESULTS

The total emissivity of different soot-covered filaments might be expected to depend on the smoothness and thickness of the deposit. The two filaments

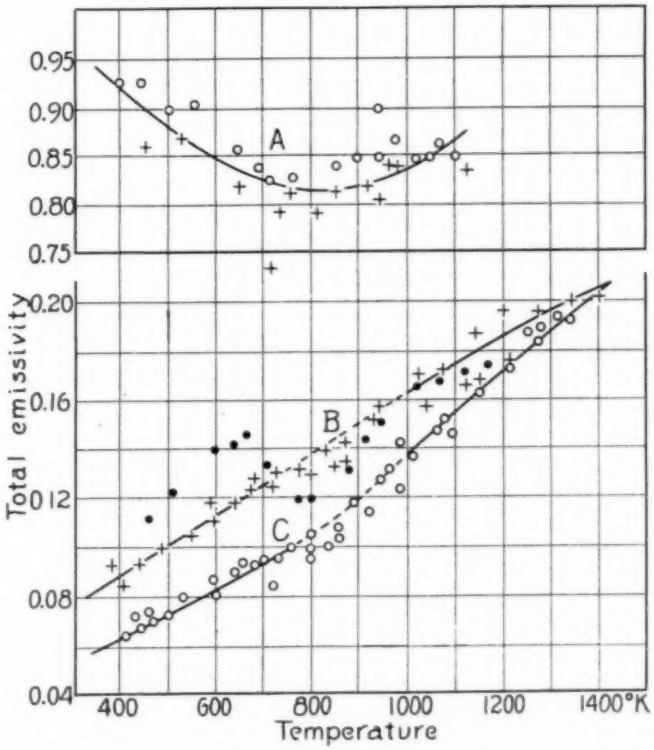

Fig. 2. Curve *A* soot-coated nickel, Curve *B* polished nickel on first heating and curve *C* same after heating to 1400°K. Dotted sections regions where temperatures were not obtained from direct measurements. Solid black circles values computed from Suydam's data.

for which data are given above were coated with a fine-grained, dull black layer a little less than 1 mil thick. According to Rubens and Hoffman[4] the optimum thickness for producing a high emissivity is of this order of magnitude. The increase in emissivity with decreasing temperature below 800°K

indicates optimum emissivity for the longer wave-lengths predominating at lower temperatures.

With polished nickel most of the observed points in the region from 800 to 900°K lie below the smooth curve drawn through the points above and below this region. Since there are no resistance-temperature data over the range from 500 to 725°C between the furnace and the pyrometer readings (dotted sections on curves of Figs. 1 and 2) the deviation of the observed emissivity values from the smooth curve is probably due to error in drawing the log-resistance vs log-temperature curves across this gap. Errors of less than 10° in the temperatures obtained from these curves would be sufficient to produce the deviation noted in the total emissivity values.

On account of inaccuracies of the temperature measurements and the possibility of end loss at the lowest temperatures measured the probable error in the emissivity values on polished nickel increases from about 1 percent in the region above 1200°K to about 5 percent at 400°K. For the soot-covered nickel the probable error in the emissivity values is somewhat larger because of difficulty in measuring the diameter and non-uniformity of the coating. It ranges from about 4 percent at 1100°K to about 8 percent at 400°K. With very uniform coating nearly the same accuracy could be expect ed with soot-covered as with polished wire.

Note added in proof.—Since sending this paper in for publication an article by C. L. Utterback has been published (Phys. Rev. **34,** p. 785, 1929) giving the relative energy radiated from nickel at temperatures ranging from 630°K to 1600°K. Data in the present paper on aged nickel agree with his results to a first approximation, giving a coefficient of 5.16 for n in the equation $E = cT^n$. The data for nickel before ageing give $n = 4.77$ as the mean value.

DIELECTRIC POLARIZATION POTENTIAL AND THE LAW OF SUPERPOSITION FOR HARD RUBBER

By Hubert H. Race and James R. Campbell, Jr.
Cornell University, Ithaca, New York

(Received August 16, 1929)

Abstract

If a constant potential E_1 is applied to an imperfect dielectric like hard rubber, there is evidence that an electrical potential E_p is built up in the dielectric. If, after a long-time charge at E_1, the applied potential is suddenly reduced to a lower value E_2, current will flow in a negative direction if E_p is greater than E_2. Therefore, a sample of hard rubber was subjected to several exactly similiar conditions of charge at $E_1 = 884$ volts per centimeter, but different conditions of discharge in that E_2 was varied from 829 to 882 volts per centimeter. The results indicate that for hard rubber the polarization potential built up during a long-time charge is approximately equal and opposite to the charging potential. Under the assumption that Curie's law of superposition held true for the existing conditions, the curve of current against time was predicted from data obtained for the same test piece over two years ago. The time when this current changed direction (measured from the instant the lower voltage was applied) was also predicted. The close correspondence between the predicted and actual curves bore out the truth of the law of superposition for the gradients used.

WHEN a continuous potential is applied across the opposite surfaces of an imperfect dielectric the total current flowing through the dielectric may be considered as being made up of three components: i_c, the current which flows by virtue of the ideal capacitance of the dielectric; i_g, the current which flows by virtue of the conductance of the dielectric; and

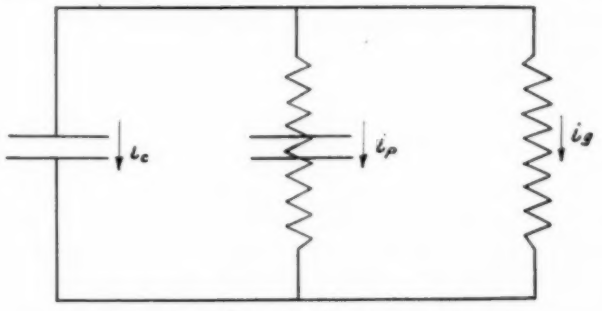

Fig. 1. Equivalent circuit for dielectric.

i_p, the current which flows by virtue of a long-time polarization of the dielectric. This last effect is not like that attributed to Debye's polar molecules because of the extreme length of time necessary to produce it. However, it must be an electric polarization because it is reversible.[1] For the above assumption the equivalent circuit may be represented by Fig. 1.

[1] S. W. Richardson, Proc. Roy. Soc. **A107**, 101 (1925).

In the tests reported in this paper, sudden changes were made in the dc potential applied to the dielectric, and the current flow in the external circuit resulting from these changes was measured as a function of time. The current i_c is a transient which becomes zero almost instantaneously, and no attempt was made to measure its value as no measurements were taken within the first half-minute after the potential was changed. As far as the experiments showed, the current i_g was independent of time and proportional to the applied potential. System leaks were of the same order of magnitude as the measured values of i_g and were included in it, so no exact statement can be made as to the value of the final conductance of the material. The work reported in this paper deals mainly with the polarization current (sometimes called absorption current), i_p, of a slab of hard rubber. Previous work on this same sample[2] has shown that

$$i_p = At^{-b} \tag{1}$$

where b is a constant and is 0.924 for this particular slab of hard rubber, and A is a coefficient directly proportional to the potential applied during charge.

If a constant potential E_1 is applied to a slab of hard rubber, the resultant current varies as a function of time according to the relation

$$i_{ch} = i_p + i_g = At^{-b} + i_g = pE_1t^{-b} + gE_1 \tag{2}$$

where p and g are the proportionality constants for the polarization and conduction currents respectively. If, now, the potential is suddenly removed, and both terminals of the test piece grounded, the discharge current is given by the relation

$$i_{dh} = -i_p = -pE_1t^{-b} \tag{3}$$

Eq. (3) states that the polarization current is reversible, as has been demonstrated by the previous experiments on this material.

There is evidence that during a long continued charge a polarization potential, E_p, opposing the applied potential, is built up within the dielectric.[1] If, then, the potential applied to the test piece, instead of being reduced to zero, is reduced to some value, E_2, lower than E_1, current will flow in a negative direction, provided E_p is greater than E_2. To obtain a value for E_p a series of runs was made for each of which the charging potential was the same ($E_1 = 884$ volts per centimeter) and the discharge potential, E_2, was varied from 829 to 882 volts per centimeter. Figure 2 shows the experimental data obtained for these runs. In each case the current was negative during a definite interval immediately after the potential was reduced from E_1 to E_2, so that E_p was greater than 99.8 percent of E_1. *This indicates that for this sample of hard rubber the polarization potential built up during a long time charge is approximately equal and opposite to the charging potential.*

[2] The previously determined data on this material and the method of current measurement is given by H. H. Race *Electric Conduction in Hard Rubber, Pyrex, Fused and Crystalline Quartz*, A.I.E.E. Jour. **47**, 788–791 (1928)

As a check on the experimental work, predicted curves based upon the law of superposition were computed, and the results compared with the observed data. This law, as given by Curie[3] in 1889, states that every variation of e.m.f. impressed on a slab of dielectric acts as though it were alone. That is, the ordinates of the curve of current as a function of time are given by the sum of the ordinates of the curves of current corresponding to the different

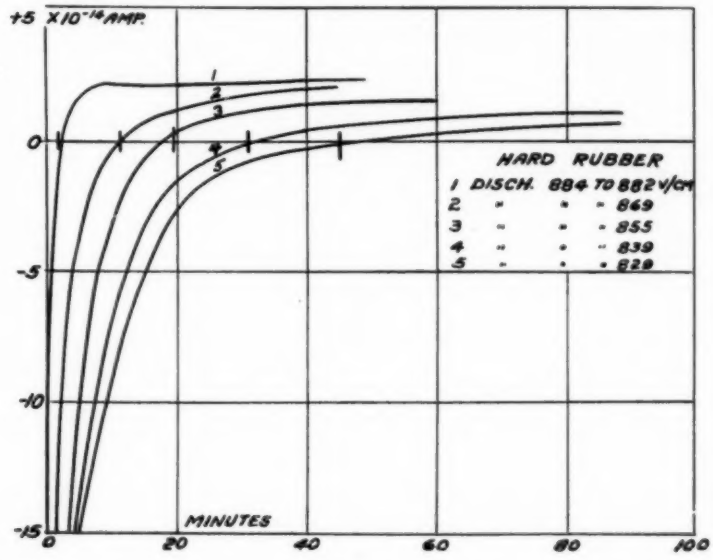

Fig. 2. Experimental data obtained when potential was reduced from E_1 to various values of E_2.

variations of emf, each variation of the emf adding to the preceding curve the curve which it would produce if it were acting alone. As a result of this last law, supported by experimental data, Curie also states that if the charging current is allowed to become constant, and the final charging current is added to each value of the discharge current, with sign reversed we obtain identically the curve of charge. Mathematically, then,

$$i_{ch} - i_g = -i_{dh}. \tag{4}$$

In cases where the potential is reduced from E_1 to some potential E_2 other than zero, the expression for the current is not Eq. (3), but

$$\begin{aligned} i &= i_1(dh) + i_2(ch) = -pE_1t^{-b} + pE_2t^{-b} + gE_2 \\ &= p(E_2 - E_1)t^{-b} + gE_2. \end{aligned} \tag{5}$$

Since $E_1 > E_2$, the first term in the right member of Eq. (5) is negative. During the time that $|p(E_2 - E_1)t^{-b}| > |gE_2,|$ i will be negative. At the instant $|p(E_2 - E_1)t^{-b}| = |gE_2|$, or when

[3] Jacques Curie, Ann. de Physique, **17**, 385 (1889).

$$t_0 = \left[\frac{p(E_1 - E_2)}{gE_2}\right]^{1/b} \tag{6}$$

the current will be zero. After this instant $|p(E_2 - E_1)t^{-b}| < |gE_2|$, and the current will be positive. The results of such calculations for one run are plotted to logarithmic scales in Fig. 3. The solid lines represent the computed values, while the dots represent experimental points.

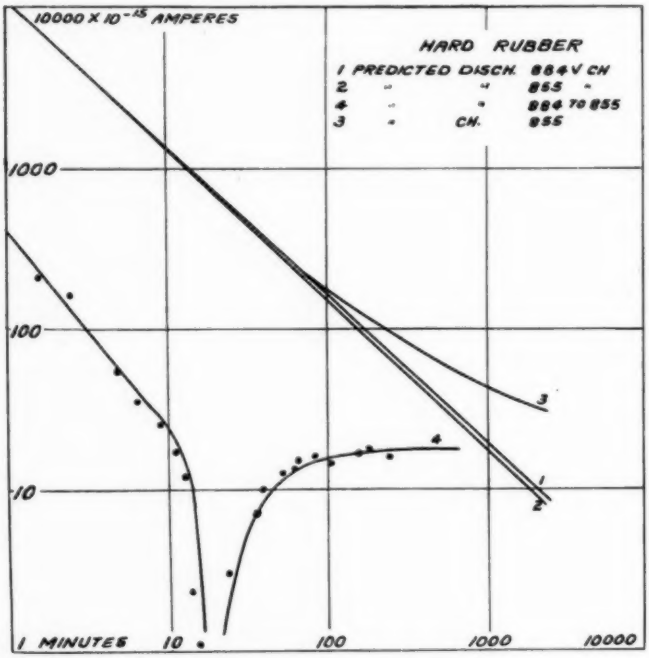

Fig. 3. Predicted and experimental curves for one run.

Using Eq. (6), which is based on the law of superposition, the instants at which the current should pass through zero in each of the runs were calculated and plotted as short vertical lines in Fig. 2. *The close correspondence between the actual and predicted curves bore out the validity of the law of superposition for the material and gradients used.*

DIELECTRIC LOSSES AT HIGH FREQUENCIES

By G. E. Owen
Randal Morgan Laboratory of Physics, University of Pennsylvania

(Received July 25, 1929)

Abstract

Description of calorimetric method and measurements of the power-loss in small pieces of dielectrics at high frequencies.—The power loss in very small pieces of dielectrics in high frequency alternating fields is measured by a calorimetric method in which the heat produced in the dielectric is compared with that produced in a resistor carrying a measured direct current. For vulcanized fibre, celluloid, rubber dam and glass the loss is found to be proportional to the frequency and to the square of the applied voltage.

THE customary methods of measuring dielectric losses at high frequency, include: (a) balanced-bridge methods; (b) electrostatic wattmeter; (c) resistance-variation method; and (d) substitution, or direct-comparison methods. In using any of these, there are difficulties, due to the assumptions that must be made. In any bridge method there are resistances and inductances whose variation with frequency is not easily determined. If an electrometer is used as an electrostatic wattmeter, a resistance is needed which should be (and probably never is) non-inductive. Likewise in a resistance-variation method, the resistance of the circuit excluding the condenser must be assumed negligible at all frequencies. In the substitution method, losses in the standard air-condenser are neglected. A method which depends upon the amount of heat generated in the condenser would seem to be clear of these difficulties. I have measured dielectric losses in gray vulcanized fibre, celluloid, dental rubber dam, and glass, by means of a differential calorimeter. This method needs no assumptions about any electrical property of the circuit and it measures only the energy transformed into heat in the condenser. It has the advantage of being applicable to small condensers which are difficult to measure by any other means.

Apparatus

Two similar two-ounce bottles, A and B (Fig. 1) are connected together through glass tubing and a specially designed manometer P, and are sealed with paraffin at atmospheric pressure. B contains a small condenser C of the substance under test and a resistor R on separate leads. The other bottle is used merely as a pressure balance to avoid the effects of external temperature and barometric changes.

The manometer consists of a circular brass case divided into two parts and flanged, so they can be fastened together with screws. A diaphragm is fastened with shellac to the projecting ring N, and the two parts are then

screwed together. Another projecting ring E, stretches the diaphragm tightly. An arm L has one end fastened to the middle of the diaphragm and the other pinned to a small rotating support for the mirror M. Good paper, thoroughly impregnated with stop-cock grease, makes a good diaphragm. Readings are taken by projecting a beam of light through the walls of the tube against the mirror, and reading the position of the reflected beam on a scale, as shown in Fig. 1. No difficulties are encountered due to distortion by the cylindrical glass walls if the plane of the mirror is approximately perpendicular to the axis of the tube.

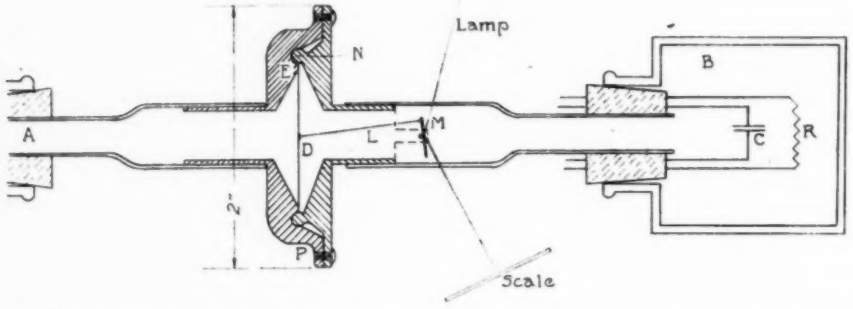

Fig. 1. Apparatus. A and B, 2-oz bottles; R, resistance; C, test condenser; M, mirror; D, diaphragm.

The electrical circuit consists of a Hartley oscillator, and a pick-up circuit made up of a coil of about 50 turns of wire across a variable air condenser in parallel with the test condenser. The pick-up coil can be moved with respect to the oscillating circuit by a slow-motion screw to obtain any desired voltage on the test condenser. The frequencies are measured with a General Radio Company wavemeter type 174B., and the voltage across the test condenser with an electrostatic voltmeter. An attempt was made to use a vacuum-tube peak-voltmeter such as is described in Van der Bijl "Thermionic Vacuum Tube," page 367, but it did not give readings which were independent of frequency. A comparison with the electrostatic voltmeter showed that at high frequencies, the tube voltmeter was entirely unreliable.

Method

When an oscillating current passes through the test condenser the heat produced in it changes the pressure of the air in bottle B. The pressure rises to a steady state, when the heat generated in the condenser is equal to that dissipated from the walls of the bottle. The deflection of the manometer beam is then noted. Afterwards the same pressure change is produced by passing a direct current through the resistor R and measuring the applied voltage with a potentiometer. The power dissipated in the condenser is then equal to that in the resistor. In practice, a curve is plotted between power used in the resistor and deflection produced. This serves

as a calibration curve for the instrument but it must be recalibrated every day. Within the range used, this curve is a straight line.

Results

Figure 2 shows the results obtained for a gray vulcanized fibre condenser 1 cm square and 0.03 cm thick, with zinc electrodes sprayed on by the Schoop pistol process. (This gives much more intimate contact between metal and dielectric than any other process available for hygroscopic materials.) The curve marked with circles is the calibration curve. It does not pass through the origin because of a slight uncertainty in the zero reading of the pressure guage. This uncertainty exists in every reading but does not affect in any way the relative values of the readings. In order to get an idea of the power-

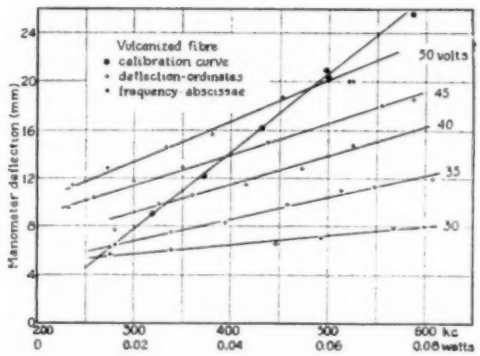

Fig. 2. Curves showing variation of dielectric losses with frequency in dry vulcanized fibre. The circles show deflection of manometer plotted against power loss in the resistor. The crosses show deflection plotted against frequency in kilocycles at various voltages. The deflections are proportional to the frequency in each case, except for the doubt due to the two points on the 50-volt curve.

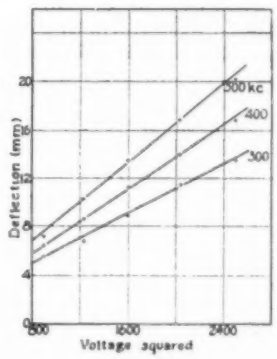

Fig. 3. Deflections plotted against voltage-squared for dry fibre. The loss is proportional to the voltage squared. Points taken from curves of Fig. 2

loss involved, we see that at 40 volts and 350 kilocycles, there is a deflection of 10 mm which is equivalent to 0.028 watts as is shown by the calibration curve. For frequencies ranging from 225 kilocycles to 600 kilocycles the power-loss is directly proportional to the frequency for voltages up to 50 volts, i.e., field intensities up to about 1700 volts per centimeter; above which the results are not consistent. This inconsistency seems to be due to some property of the condenser, as it was found in rubber and celluloid but at different voltages. The dielectric loss is proportional to the square of the voltage for all frequencies in the range tested. This is shown in the curves of Fig. 3, whose points were taken directly from Fig. 2.

The presence of moisture has a very large effect. A condenser kept in an atmosphere of about 70 percent relative humidity over night showed twice as much loss as a similar one kept for two days in a bottle containing

a little phosphorus pentoxide. The condenser which gave the curves used in this article had been kept in a sealed bottle containing phosphorus pentoxide for over two months. For several weeks there was a noticeable decrease in the deflections, indicating that the drying-up process may extend over a long period of time. A condenser kept in a bottle containing a few drops of water gave very large deflections which were not reproducible.

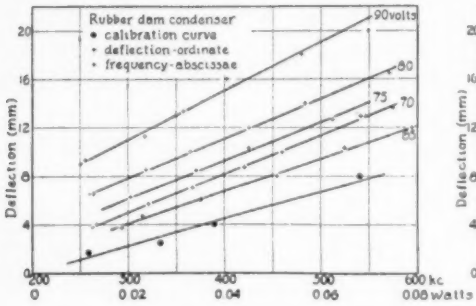

Fig. 4. Rubber dam condenser, 2.5 cm square and 0.03 cm thick. The loss is proportional to frequency up to 90-volt curve.

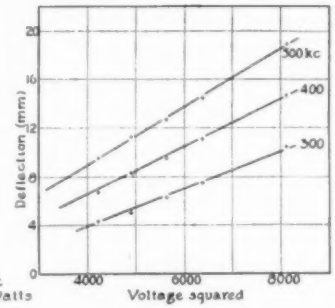

Fig. 5. Rubber dam condenser. Deflections of manometer plotted against voltage squared. Points taken from Fig. 4. The power loss is proportional to the square of the voltage at each frequency.

Condensers of white celluloid and dental rubber dam were tested with results which may be summarized as follows. For all voltages which gave consistent readings, the losses bear a linear relation to the frequency and vary as the square of the voltage. The readings for celluloid become incon-

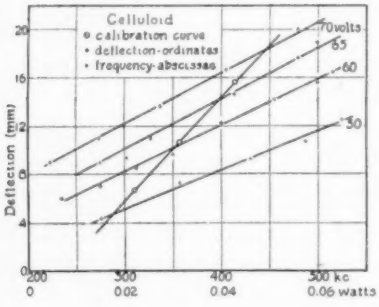

Fig. 6. Celluloid. The loss is proportional to the frequency up to 70 volts for a celluloid condenser 2 cm square and 0.03 cm thick.

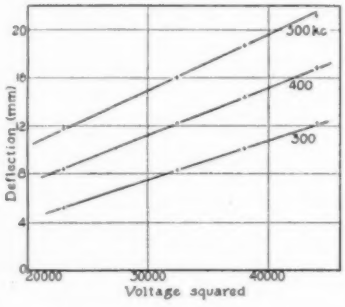

Fig. 7. Celluloid condenser. Deflections plotted against the voltage squared. The power loss is proportional to the square of the voltage.

sistent at about 200 volts, i.e., about 7000 volts per centimeter and for rubber at about 90 volts or 3000 volts per centimeter. A small microscope coverglass used as a condenser showed losses proportional to the frequency at

about 250 volts. Higher voltages were not available but the work will be continued on this and on clear fused quartz which also has been found to have a measurable loss.

Comparison of Results with Previous Work

It is not easy to compare these results with those of others, because most of the work done at high frequencies has been reported in terms of the power-factor of the condenser. It is generally accepted that the ratio S/cp is equivalent to the power-factor, where S is the conductivity of the dielectric at the frequency used, c is the capacity and p the frequency. But every term in this expression depends on the frequency and therefore the curves plotted between power-factor and frequency are not simple in form. Dr. G. E. Bairsto[1] has measured the conductivity of a variety of substances and finds, in most cases, one or two maxima in the curves plotted between conductivity and frequency. My results on similar substances show no evidence of such maxima. DuBois[2] finds the loss varies as the frequency

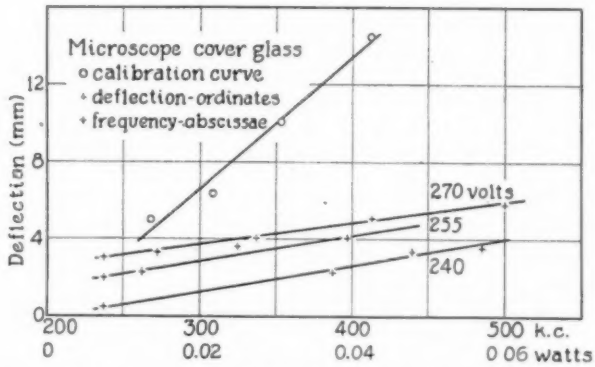

Fig. 8. Shows how the manometer deflection varies with frequency for a condenser made from a small microscope cover glass. The deflections are very small but seem to bear a linear relation to the frequency.

for low moisture content. While several observers have reported that dielectric losses in many insulators are proportional to the square of the voltage, the results of C. A. Butman[3] at low frequencies do not lead to that conclusion. Also James Mould[4] reports, "Energy dissipation varies as some power of the electric force which is greater than the square. The exponent varies greatly but is always greater than two." He also reports that in so-called "good insulators" the exponent varies greatly from two.

My results show the loss porportional to the square of the voltage up to a certain voltage for each material. It is possible that some change takes place in the dielectric or in the nature of the discharge through it, near voltages at which my results become inconsistent.

[1] G. E. Bairsto, Proc. Roy. Soc. London, **96**, 363 (1919).
[2] D. DuBois, J. A.I.E.E., page 689 (1922).
[3] C. A. Butman, Electrical World, **71**, 502 (1918).
[4] James Mould, Beama, June, 1923.

A STATIC BALANCE ELECTROMETER METHOD OF MEASURING DIELECTRIC CONSTANTS OF ELECTROLYTES

By A. P. Carman, O. B. Young, and K. O. Smith
University of Illinois, Urbana

(Received August 19, 1929)

Abstract

The differential idiostatic electrometer method devised by A. P. Carman has been arranged so that readings can be made with conducting electrolytes by static balance. The thermal disturbances have been controlled by a special cooling water jacket, around the vessel containing the tested solution. A diagram showing the connections and special arrangements is given.

THE differential electrometer method[1] of measuring the dielectric constants of liquids was first used with liquids of poor conductivity such as water and alcohol. When electrolytes of considerable conductivity are used,

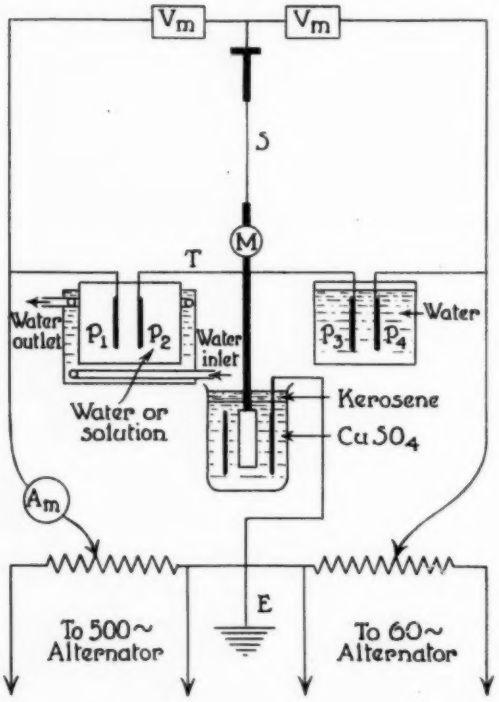

Fig. 1. Arrangement of apparatus.

the electric currents between the plates of the electrometer cause serious thermal disturbances. To avoid these disturbances Schmidt[2] used the device of first-throw readings, thus taking readings rapidly and assuming

[1] A. P. Carman, Phys. Rev. **24**, 396 (1924).
[2] C. C. Schmidt, Thesis deposited in University of Illinois Library, May 15, 1927; A. P. Carman and C. C. Schmidt, Phys. Rev. **30**, 922–930 (1927).

constancy of conditions for the short time of the observations. This method of first-throw readings and instantaneous balance is, however, open to serious objections and therefore a method of static balance has been developed. Several changes in the apparatus and connections have also been made. In describing the method, Fig. 1 will be useful.

The needle system consists of the bar T, carrying the platinum plates P_2 and P_3. The fixed plates P_1 and P_4 are placed so as to produce equal opposing torques or balance on the needle system. The differences of potentials between the two pairs of plates immersed in water are respectively V_1 and V_2. When one pair of plates is immersed in water and the other pair in the solution, the balancing potentials are V_1' and V_2'. It is easy to deduce the relation

$$\frac{k'}{k}=\left\{\frac{V_2}{V_1}\right\}^2 \div \left\{\frac{V_2'}{V_1'}\right\}^2$$

where k and k' are respectively the dielectric constants of water and of the solution.[3] The importance of the potential readings is seen directly from the above equation.

One of the immediate effects of heating the electrolyte is to change its electrical resistance, and thus to change the difference of potentials between the plates. Hence a first problem in a static balance is to control the temperature of the solution under test. This was done by surrounding the walls and bottom of the thin glass vessel containing the solution, with a metal jacket, through which a continuous stream of water flows. The glass vessel was sealed tightly in this jacket by tape and asphalt. The water came from a large elevated tank in which the level was kept constant. The solutions of concentrations below 0.012 normal solution were cooled by having tap water stored in the tank flow through the jacket. Ice was used in the tank water for higher concentrations in which more heat was generated. Convection currents in the solution at first disturbed the balance of the immersed plates. These convection currents were due to temperature gradient when the cooling water entered at one side of the jacket and escaped at the other side. This difficulty was completely overcome by admitting the cooling water through numbers of small holes in a copper tube at the bottom of the jacket, and allowing this water to escape through holes in a similar ring tube at the top of the cooling jacket. A copper-constantin thermocouple, enclosed in a thin glass tube, gave the temperature of the solution between the plates. These temperatures were read to two-tenths of a degree Centigrade. By this arrangement it was possible after practice to maintain the temperature of the solution practically constant for almost any time. With thermal equilibrium in the solution under test, it is thus possible to get a sensitive balance with conducting solutions as definite and stable as with a non-conducting liquid. A number of new arrangements are shown in the figure and need not be described further.

[3] E. B. Rosa (Phil Mag. (5) **31**, 188 (1891)) in his valuable pioneer work on the dielectric constants of electrolytes proved experimentally the theoretical relation, $F=AKV^2$, for the force between immersed plates, showing also that the force does not depend on the electric currents passing.

THE DIELECTRIC CONSTANTS OF THREE ELECTROLYTES BY A STATIC BALANCE ELECTROMETER METHOD

By A. P. Carman and K. O. Smith
University of Illinois, Urbana

(Received August 19, 1929)

Abstract

Values of the dielectric constants of solutions of KCl, $CuSO_4$ and $BaCl_2$, are measured for normal concentrations of from 0.001 to 0.024 at temperatures between 25°C and 26°C, and in fields of about 26.7 volts. The results are given in table and curves. The dielectric constants of dilute solutions are found to increase at first above that of water, and later to decrease. In the case of $CuSO_4$, the dielectric constant is greater than that of water. The results are consistent to one percent of the mean, and have a probable accuracy of less than two percent. The results are in general confirmation of those of J. F. Smale for dilute solutions.

THE purpose of the investigation was to measure the dielectric constants of several typical electrolytes under conditions of controlled temperature and particularly at higher concentrations. It was necessary to use a "force" method for the higher concentrations, and the static balance electrometer method as described elsewhere[1] was chosen.

In the electrometer method it is very important to maintain very constant potentials. For these potentials, two motor generators were used, a 0.5 KW Crocker-Wheeler 500 cycle machine and a 2 KW Holzer-Cabot 60 cycle machine. The 500 cycle alternating potential was used across the electrolytic solution, and the 60 cycle potential across the pure water. No

Table I. *Sample set of readings.*
Water on each side of electrometer

Time	V_1	V_2	Temp. °C	Ratio V_2/V_1
12:30	24.65	26.95	26.6	1.093
12:40	24.65	26.95	26.6	1.093
12:50	24.50	26.92	26.6	1.098
12:55	24.40	26.90	26.6	1.102
	Avg. $V_2/V_1=1.096$; $1.096^2=1.201$			
	KCl, 0.004 normal solution, on second side			
Time	V_1'	V_2'	I (amp.)	Temp. °C	Ratio V_2'/V_1'
1:55	25.0	26.6	0.2	26.6	1.064
2:00	25.0	26.56	.2	26.2	1.062
	Avg. $V_2'/V_1'=1.063$; $1.063^2=1.130$				

$$\frac{k'}{k}=\left\{\frac{V_2}{V_1}\right\}^2 \div \left\{\frac{V_2'}{V_1'}\right\}^2=\frac{1.201}{1.130}=1.063.$$

polarization could be detected at any time. The motor generators were driven by current from the 300 ampere-hour storage battery of the department. The machines were generally run a half hour before beginning read-

[1] Carman, Young and Smith, Phys. Rev. preceding paper in this issue.

ings, so as to get steady conditions. These voltage sources were so constant that any change was seldom observable on voltmeters which could be read easily to tenths of a volt. The potential differences at the plates were measured by two Weston thermo-voltmeters of resistances of 3750 and 6250 ohms respectively. These instruments were correct for our frequencies. As the voltages used were very nearly the same on both pairs of plates, and calculations are made from voltage ratios, the readings of these voltages were much more accurate than required for our purposes.

The procedure of the observation can be seen from the sample set of readings and calculations shown in Table I.

The final results for solutions of KCl, $CuSO_4$ and $BaCl_2$, are given in Table II, and shown in the curves of Fig. 1.

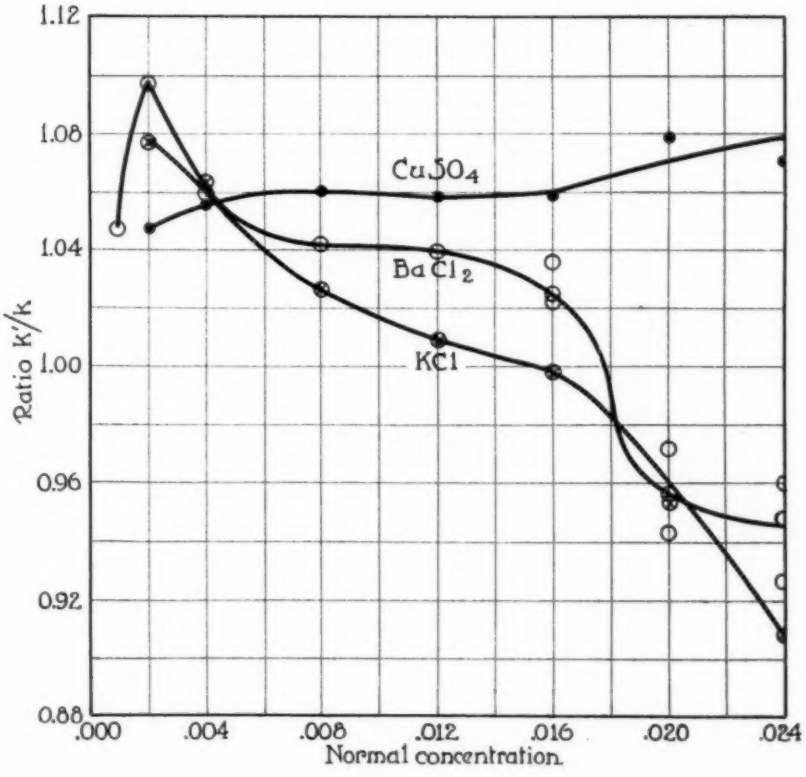

Fig. 1. Dielectric constants of solutions of KCl, $CuSO_4$ and $BaCl_2$.

The set of data for each point of the curve was obtained with conditions as nearly constant as possible. The temperature variation was between 24°C and 27°C, most of the points being obtained with the solution between 25°C and 26°C. This was very necessary as any temperature change produces a marked effect. All points on the curves are for approximately the same field intensity. The potential differences of the plates in the solution varied from 26.13 to 27.06 volts, most of the points being for 26.7 volts. The plate distances were unchanged during the work, a desirable setting of the plates having been found by trial. A change of 0.1 volt on the plates immersed

TABLE II. *Dielectric constants of solutions of KCl, $CuSO_4$ and $BaCl_2$*

Normal Concentration	Ratio of Dielectric Constant of Solution to that of Water	Normal concentration	Ratio of Dielectric Constant of Solution to that of Water
KCl		$BaCl_2$	
0.002	1.076	0.001	1.046
.004	1.063	.002	1.098
.008	1.026	.004	1.060
.012	1.010	.008	1.042
.016	.999	.012	1.039
.020	.955	.016	1.036
.024	.910		1.027
			1.024
$CuSO_4$			
.002	1.047	.020	.972
.004	1.057		.945
.008	1.060		.958
.012	1.059	.024	.949
.016	1.059		.960
.020	1.079		.929
.024	1.072		

in water caused a 10 mm shift of the balance reading. When the voltage connection was broken, there was no appreciable shift, showing that convection currents in the solution had negligible effects. Since only a few points on a curve could be obtained in one night, the stability of balance was important. Thus curves for KCl, and $CuSO_4$ show no irregularities, even where the parts were taken on different days.

In the curve for solutions of $BaCl_2$, the dielectric constant decreases rather rapidly between the concentrations 0.002 and 0.016. There was some difficulty in obtaining the point for the concentration 0.016, as the results seemed very dependent on temperature. The data for the concentrations 0.016, 0.020 and 0.024 were taken three times, several days intervening each time. The maximum difference from the mean was less than 1.1 percent.

From the tables of data it is found that results obtained from continuous runs of observation are consistent with each other within one percent. Great care was taken to reproduce conditions, where runs of observation had to be made on different days, and these repeated observations show a maximum variation of about one percent. We feel safe in saying that the results for the same conditions are not in error by more than two percent. The above results thus give the dielectric constant for dilute solutions as greater than the dielectric constant of water. This result was unexpected by us and has therefore been subjected to the most careful scrutiny for errors. The result is in general agreement with work of Smale.[2] Smale's work was done in Nernst's laboratory by a Nernst electrometer method, and evidently with care. Most of the results of later observers have not agreed with Smale; but temperature has a big effect on dielectric properties of solutions, and in numbers of cases the temperature has not been closely controlled.

There is certainly need of much additional data on the relation of dielectric constants, concentrations and solutions before we can have an acceptable theory of electrolytic solutions. The curves given above show that the interactions of the ions or dipoles are large and probably not simple.

[2] J. F. Smale, Ann. d. Physik **60**, 625 (1897).

THE ABSORPTION OF ULTRA-VIOLET LIGHT BY OXYGEN, WATER VAPOR AND QUARTZ*

By L. P. Granath
Naval Research Laboratory, Washington, D. C.

(Received August 19, 1929)

Abstract

Quantitative measurements were made of the absorption of light by oxygen, water vapor and crystalline quartz in the spectral region 1850 to 2300A, by means of a quartz spectraph and a recording densitometer. Defining the absorption coefficient α by $I = I_0\, 10^{-\alpha d}$ where d is the distance in cms, values of α were obtained for oxygen at atmospheric pressure in tubes up to 5 meters in length, which showed the peaks of absorption due to the Schumann-Runge band system below 1970A. From 2000 to 2100A the absorption appeared continuous with no marked peaks, α being 0.00025, 0.00032 and 0.00050 at 2100, 2050 and 2000A respectively. The values of α for saturated water vapor at 25°C were 0.0005, 0.0013, 0.003 for wave-lengths 2050, 1950 and 1900A. For a specimen of crystalline quartz 2.5 cm thick α was found to be 0.086, 0.11, 0.13 and 0.17 for wave-lengths 2040, 2000, 1940 and 1870A.

IN THE present investigation the light absorption coefficients of oxygen, water vapor and crystalline quartz have been measured in the spectral region from 2300 to 1850A. Kreusler[1] obtained the absorption coefficients of oxygen at 1860 and 1930A, and Pflüger[2] and Tsukamoto[3] made measurements on crystalline quartz from 2100 to 1850A. No measurements on water vapor seem to be available.

The transmissions of the various substances under investigation were measured by the photographic method described by Ham, Fehr and Bitner[4] and others. By means of a quartz spectrograph, five exposures of equal time were made on the same plate, four with wire screens having transmissions of 100 (no screen) 58, 32 and 15 percent inserted between the spectrograph and the source, and the fifth with the absorbing substance. The opacities of the lines in the five spectra were measured by a recording densitometer. Several prominent lines were selected in the region under investigation and the opacities of these were plotted as functions of the transmission. Then knowing the opacity of each line in the spectrum taken through the absorbing substance the corresponding transmission could be obtained. The absorption coefficient α defined by the equation

$$I = I_0 10^{-\alpha d} \tag{1}$$

where I/I_0 is the transmission and d is the thickness of the absorbing substance in centimeters was calculated from the observed transmission. Wire screens

* Published with permission of the Navy Department.

[1] H. Kreusler, Ann. d. Physik **6**, 412 (1901).

[2] A. Pflüger, Phys. Zeits. **5**, 215 (1904).

[3] M. K. Tsukamoto, Rev. d'Optique **7**, 89 (1928).

[4] Ham, Fehr, Bitner, J. Frank. Inst. **178**, 299 (1914).

ranging from 18 to 150 mesh per inch calibrated in the ultra-violet by means of a monochromatic illuminator and a quartz photoelectric cell, and in the visible by a Nutting spectrophotometer, were used to calibrate the plates, the conditions under which the screens were calibrated were made as nearly identical as possible to those under which they were used. The transmission of each screen was found to be constant from 2536 to 4046A and in the visible within the limit of error which amounted to about 3 percent. Below 2536A the transmission was not measured, but was assumed to be the same as that of the longer wave-lengths. As Schumann plates required a less time of exposure than ordinary plates in the region 1850–2000A they were used in all cases except for the 11.7 cm piece of quartz. Due, however, to the irregularities and large grain structure in the emulsion, the errors in the transmis-

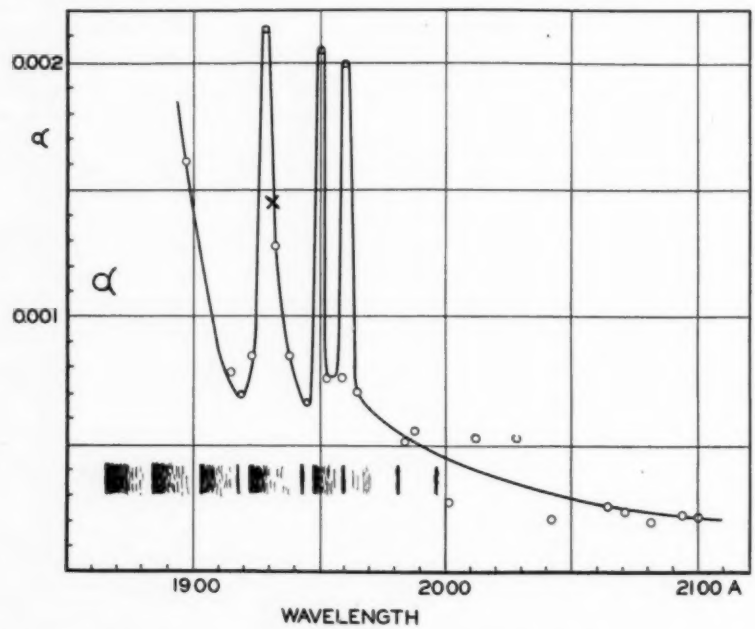

Fig. 1. Light absorption coefficient α of oxygen. Circles indicate values obtained in present investigation, while the cross indicates the value found by Kreusler.

sion values obtained from these plates amounted to about 10 percent. A condensed iron spark was used as a source in the measurements on oxygen and a silver spark on water vapor and quartz.

Oxygen. Commercial oxygen, purified with heated platinum black and phosphorus pentoxide, was passed into the absorption chamber which previously had been thoroughly evacuated and dried. The absorption chamber consisted of a Pyrex tube 3.5 cm in diameter and 511 cm long; quartz windows were fastened on the ends with sealing wax. Four calibration spectra were taken through the evacuated tube and a spectrum through the tube filled with oxygen at atmospheric pressure. The values of α for oxygen are shown in Fig. 1, by the circles and smooth curve. The cross is the value given

by Kreusler.[1] The Schumann-Runge band absorption system of oxygen, including a few lines of undetermined origin, is sketched in Fig. 1 from a plate taken with a five meter thickness of oxygen using the continuous spectrum of mercury as a source in this region. The wave-lengths of the heads of the bands agreed with those given by Duclaux and Jeantet,[5] S. Leifson[6] and by L. and E. Bloch.[7] The curve for α gives only a partial reproduction of the bands, it cannot be considered as a complete absorption curve which gives all the details of the band structure. For this purpose greater dispersion and

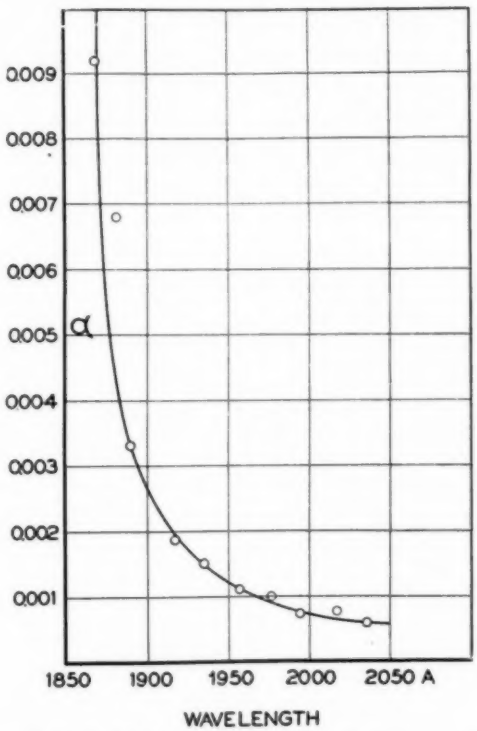

Fig. 2. Light absorption coefficient α of water vapor.

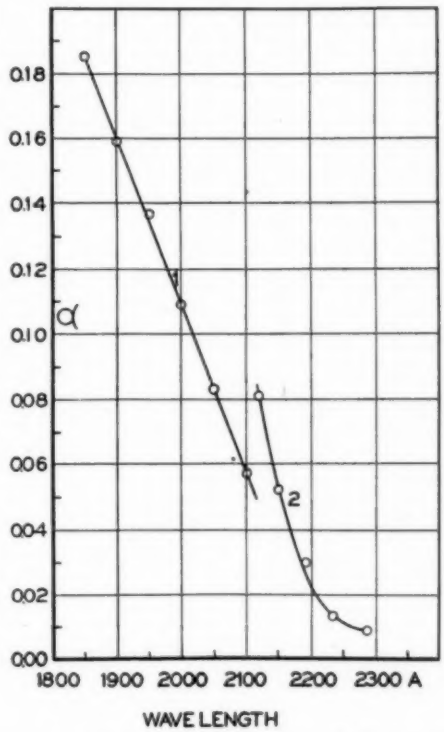

Fig. 3. Light absorption coefficient α of quartz; curve 1 represents values for a 2.5 cm piece of quartz and curve 2 values for a 11.7 cm piece.

a more extended series of observations would be necessary. For example it was noticed that two iron lines at about 1959 and 1960A were of approximately the same intensity when the tube was evacuated, but when the tube was filled with oxygen λ1951 almost vanished whereas λ1950 was little changed.

Water vapor. The values of the absorption coefficients of water vapor are given in Fig. 2. To obtain these the exposures were taken with the various

[5] Duclaux and Jeantet, Comptes rendus **173,** 581 (1921).
[6] S. Leifson, Astrophys. J. **63,** 73 (1926).
[7] L. and E. Bloch, Comptes rendus **158,** 1161 (1914).

screens through the evacuated and thoroughly dried tube; the tube was then connected with a bulb containing distilled water, the bulb being slightly heated until enough vapor entered the tube to condense on the walls. The windows were heated with a flame in order to remove any condensed water, the slight heating kept them dry for a longer time than was necessary for the exposure. A path of 241 cm was used for the absorption from 2050 to 1920A, and from 1920 to 1860A the path was 29 cm.

Quartz. Measurements were made on two pieces of crystalline quartz, optically good, one 2.5 cm and the other 11.7 cm thick. In order to obtain consistant results it was found necessary to clean carefully the quartz with alcohol before each set of exposures. Fig. 3, curve 1 gives the values of α, corrected for surface reflection for the 2.5 cm piece and curve 2 for the 11.7 cm piece. In the spectrum region around 2100A where the two curves can be compared, they show different values of α, this was a real difference in the two pieces of quartz. Tsukamoto[3] also found different absorption values for various samples of quartz.

It is of interest to calculate the absorption of ultra-violet light in a quartz spectrograph. For example, the small quartz spectrograph, Hilger type E31, has two quartz lenses of a total thickness of 0.55 cm, a 60° quartz prism whose base measures 2 cm approximately, and an air path of about 40 cm from the slit to the photographic plate. It was found by calculation from the data of Figs. 1 and 3 that for λ1860 the absorption of the quartz in the spectrograph was 50 percent and of the air was 17 percent. For λ1900 the respective values were 31 and 3 percent, for λ2000 23 and 1 percent and for λ2100 16 and 0.5 percent.

In conclusion the writer wishes to thank Dr. E. O. Hulburt, who suggested the problem, for his interest and help during the investigations.

REMARKS ON "THE EFFICIENCY OF QUENCHING COLLISIONS AND THE RADIUS OF THE EXCITED MERCURY ATOM"[1]

By E. Gaviola
Department of Terrestrial Magnetism, Carnegie Institution of Washington

(Received August 26, 1929)

Abstract

It is shown that the interpretation given to the reabsorption-factor f in the previous publication was erroneous. An improved and general treatment of reabsorption is given in which the radius of the excited mercury atom turns out to be 3.4A for hydrogen and 5.7A for CO collisions. The efficiencies of collisions with other gases are 0.4 for H_2O, 0.2 for N_2, 0.05 for A, and 0.005 for He.

PROFESSOR Peter Pringsheim kindly called my attention to the fact that the interpretation given to the reabsorption-factor f in the publication mentioned above is erroneous. In fact f is always to a first approximation equal to one-half for the case considered, as calculated by Foote[2], and it does not depend on the foreign gas-pressure. The paragraph of the previous publication regarding the factor f and the diameter of the excited atom has to be modified therefore in the following form.

Let us consider a vessel containing mercury vapor illuminated by parallel light of 2537A through a plane quartz-glass window and observed from a direction differing only slightly from the one of illumination. Let us consider

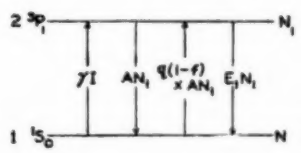

Fig. 1

further a cylindrical volume element of small section and indefinite length, placed at the center of the illuminated zone with its axis parallel to the light beam. Let γI be the number of light quanta absorbed per second in our cylinder out of the primary light. If N_1 is the number of resonance atoms in it AN_1 quanta will be emitted per second (A = transition probability) out of which only fAN_1 will leave the vessel in the direction of observation. The rest of them $(1-f)AN_1$ will be reabsorbed in the vessel but most of them in other volume elements and not in the one we are considering. If the illuminated surface is larger than the section of our cylinder, this last will

[1] E. Gaviola, Phys. Rev. **33**, 309 (1929). Referred to as l.c. in the following.
[2] P. D. Foote, Phys. Rev. **30**, 288 (1927).

absorb on the other hand part of the radiation emitted by the surrounding volume. In the case of equilibrium of radiation the number of quanta given by our volume element to the surroundings will be equal to the number absorbed by it from the surroundings and this number will be $(1-f)AN_1$. In the general case when there is no equilibrium only a part q of this will be reabsorbed. The ratio q is a number which is equal to zero if the illuminated zone is very small and equal to one if it is very large, and it will have values between these two limits in the general case.

Therefore (Fig. 1)

$$\gamma I+q(1-f)AN_1=AN_1+ZE_1N_1 \tag{1}$$

and if we make

$$AN_1/\gamma I=J/(1-q(1-f)) \tag{2}$$

then

$$J=1/[1+(ZE_1/A(1-q(1-f))] \tag{3}$$

is the general formula for the quenching of resonance radiation by hydrogen. For $q=0$ we obtain the expression used by Stuart[3] and for $q=1$ Foote's formula (3). We can obtain an idea of the numerical values of q by considering the following examples: If the illuminated section is circular and has a radius of 5 mm and if we observe the radiation emitted by the center of it, then $q=1/2$ (because resonance radiation is decreased to 1/2 in 5 mm mercury vapor); if the radius is only 2.5 mm, then $q=1/4$; for radius $=1$ cm, $q=3/4$, and so on. As stated before $f=1/2$ for all foreign gas pressures in first approximation as calculated by Foote, therefore

$$J=1/[1+(ZE_1/A(1-q/2))]. \tag{4}$$

If we calculate now the collision radius of the excited Hg atom using formula (4) applied to the half pressure 0.217 mm found by Stuart for hydrogen and assuming an efficiency $E_1=1$ for H_2 collisions we obtain for the sum σ of the radii of the hydrogen molecule and the excited mercury atom

$$\sigma=4.8(1-(q/2))^{1/2}\cdot 10^{-8}\text{ cm}$$

and putting for H_2 the gas kinetic radius $r_{H_2}=1.09\cdot 10^{-8}$ we find

$$r_{Hg'}=[4.8(1-(q/2))^{1/2}-1.09]10^{-8}\text{ cm}. \tag{5}$$

The value of q depends on the geometrical arrangement of the experiment. I will assume that in the case of Stuart, q was of the order of magnitude of 1/4. Then

$$r_{Hg'}=3.4\cdot 10^{-8}\text{ cm}$$

the radius of the excited mercury atom for hydrogen collisions.

[3] H. Stuart, Zeits. f. Physik **32**, 262 (1925).

The method and considerations applied in the previous paper for the calculation of the efficiency of collisions with other foreign gases remain valid; only formula (6) l.c. has to be replaced by

$$E_1=(1-(q/2))A(1-J)/JZ \qquad (6)$$

and the numerical values obtained for the efficiencies E_1 have to be modified owing to the new value for r_{Hg}' in the case of H_2, to the more correct interpretation of f, and to the introduction of the factor q. The following tables I and II take the place of the ones in the previous paper.

TABLE I.

Gas	Radius	$Z(r_{Hg'}=3.4A)$	Efficiency $p\to 0$	$Z(r_{Hg'}=5.7A)$	Efficiency $p\to 0$
H_2	$1.09\cdot10^{-8}$ cm	$3.75\cdot10^7$ p	1	$8.5\cdot10^7\,p$	0.44
H_2O	1.36	1.46	0.17	3.3	0.076
N_2	1.58	1.3	0.08	2.8	0.037
A	1.43	1.05	0.025	2.3	0.011
He	1.00	3.6	0.002	8.3	0.00086
CO	1.6	1.3	2.15	2.8	1

TABLE II.

Gas	Radius	$r_{Hg'}$	Z	E_1
CO	1.6A	5.7A	$2.8\cdot10^7\,p$	1
H_2	1.09	3.4	3.75	1
H_2O	1.36	1.8	0.64	0.4
N_2	1.58	1.8	0.6	0.2
A	1.43	1.8	0.5	0.05
He	1.00	1.8	1.4	0.005

The curves of Figures 4, 5, and 6 (l.c.) are only slightly modified by the new results. They conserve their general form. We see that the new values for the efficiencies are in most cases the same as calculated before, the new Z values are but slightly different.

DEFINITION OF FREQUENCY

By John Q. Stewart
Princeton University

(Received June 15, 1929)

Abstract

If energy applied to change the moment of inertia of a rotating bar is taken as the analogue of work in thermodynamics, and energy applied to change its speed of rotation as the analogue of heat, then frequency is the analogue of absolute temperature, and can be defined by a process exactly corresponding to that by which absolute temperature is defined. The second law of thermodynamics is thus symbolically equivalent to a principle of mechanics. This paper illustrates the possibilities of purely formal studies of physical principles.

HELMHOLTZ[1] and Hertz[2] have dealt with some of the analogies between "monocyclic systems" in mechanics and the "working body" in thermodynamical problems. Their investigations were guided by the idea that apparently non-mechanical forms of energy, such as heat, are to be exhibited as ultimately mechanical; and that a wide range of physical phenomena are to be included within the domain of mechanics.

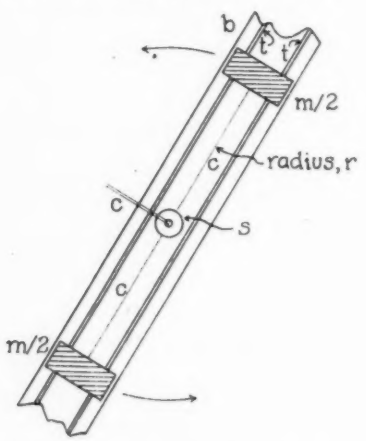

Fig. 1. Model for "working body."

In the present discussion the argument is inverted, and the thermodynamical pattern is taken as the prototype of mechanical theory. This proposition and a few of its corollaries have been advanced in papers before the American Physical Society.[3]

Imagine an observer who has clear ideas of the principles of statics, but none of dynamics, and who has no clocks and only a vague notion of time.

[1] H. L. F. von Helmholtz, *Wissenchaftliche Abhandlungen*, v. 3, p. 142, 1895.
[2] H. R. Hertz, *The Principles of Mechanics*, p. 209, 1899.
[3] J. Q. Stewart, *Phys. Rev.* **33**, 637, 641 (1929).

He is provided with means of measuring distances and forces, and so of mechanical work. (He might be a contemporary of Galileo, unaware of the latter's studies.) Suppose that he stands at a long table, out of which protrude the ends of a number of shafts which rotate without friction at various frequencies. We may suppose these shafts attached to concealed flywheels, having large moments of inertia.

Someone has constructed for him the "working body" of Fig. 1. The bar b, of indefinite length, carrying the tracks t, rotates in the horizontal plane about the vertical shaft s, to which b is rigidly attached. Two cars, each of mass $m/2$, move on the tracks, being kept by the flexible cords c at equal distances r from the center. The cords c pass through the sides of the shaft to pulleys, and then along inside the shaft, emerging from one end. The bar b is supposed rotating, and a force F is applied to the cords from without to just balance the centrifugal force. Friction is altogether neglected and for simplicity the bar, tracks, and shaft are assumed to possess negligible mass.

Our ignorant observer may be unaware of the motion of the bar, as the latter may be supposed concealed in a box, leaving visible only the vertical shaft and the cord. He realizes, however, that energy may be communicated to the system in two ways—as mechanical work, "energy of pull," through motion of the cord (measured by force times distance), or as "energy of twist," by applying a moment of force to the shaft (measured by moment times angular displacement.)

The latter is the analogue here of heat in the thermodynamical argument. Frequency is the analogue of temperature. When two bodies have the same temperature, no heat flows if they are placed in thermal contact. Similarly two shafts have the same frequency if no energy of rotation passes when they are clamped together through a machine which measures energy communicated through the action of a moment of force. (Such a machine can readily be devised; it would resemble a dynamometer, but its employment would not involve measurement of time.)

The simple "working body" of Fig. 1 consequently may be employed, (like a mercury or alcohol thermometer) to determine the *order* of frequencies of the various shafts, from low to high. This is accomplished by noting the length of cord x, which extends outside the box when the shaft of the "working body" is brought to the frequency of a given shaft— a constant pull F being maintained on the cord, by means which need not be specified here. The "working body" may be brought to any frequency if its shaft is clamped to that of a large flywheel of variable frequency—just as the temperature of a thermometer is changed by altering the temperature of the chamber in which it is placed. Used in this way the "working body" may be called a "string frequency meter;" but its readings are not of absolute frequencies, as the length of cord measured is not a function of frequency only.

The observer plots curves on the "F, x" diagram which define the properties of the "working body," indicating frequencies as measured on his arbitrary scale. Here F (centrifugal force) is analogous pressure, and x (length

of cord) is analogous volume. When the shaft is insulated from the other shafts, variation of F gives the "adiabatic" transformation. When the shaft of the working body is clamped to another shaft of coincident frequency, driven by a very large flywheel, variation in F gives the analogous isothermal change.

When the frequency of the large flywheel is varied, the change in frequency corresponding to the communication of measured energy of rotation determines the " capacity" of the working body for energy of rotation— at constant x or at constant F.

Also the "working body" may be used as an engine, converting energy of rotation into mechanical work—operating, for example, along the analogous Carnot cycle. Energy of rotation Q_1 is taken in at constant frequency f_1 from the shaft which serves as source; and Q_2 is delivered to a sink at f_2. The net work performed per cycle is

$$w = -\int F dx = Q_1 - Q_2, \tag{1}$$

where the integral is around the cycle. This equation embodies the principle of the conservation of energy in transformations between the "twist" and "pull" forms—the "first law."

The *efficiency* may be defined as w/Q_1. By trial the observer will find that the efficiency (for ideal frictionless engines) is a function only of the frequencies of source and sink.

To justify this empirical result he may formulate the "second law." *By reversible cyclical processes energy of rotation is not transferred without compensation between shafts at different frequencies.*

Then employing the familiar reasoning of Kelvin he will establish an "absolute scale" of frequency. He will be able to tag each shaft with a number expressing its frequency, in terms of the difference of frequencies of two arbitrarily chosen standard shafts as unit. Thus with neither clocks nor a clear idea of time he has reached a precise measure of frequency.

He notes that the increment of rotational energy, dQ and of mechanical energy, dW (work done on the system), are not in general perfect differentials. The first law is that

$$dU = dQ + dW, \tag{2}$$

where dU is a perfect differential. That is, U is a function only of the variables F and x which define the state of the system.

In consequence of the "second law", for reversible systems,

$$dJ = dQ/f,$$

where dJ is a perfect differential, being the increment in analogous entropy, and f is the "absolute" frequency. Thus the "second law" leads to a definition of frequency as an integrating factor. The additional definition is involved,

$$dW = Fdx = -Fdr, \tag{3}$$

where r is the radius (Fig. 1).

Justification of the above statements concerning the results of the hypothetical experiments rests on the following equations of elementary mechanics:

$$F = 4\pi^2 mrf^2 \; ; \quad U = 2\pi^2 mr^2 f^2 \; ; \quad dQ = dU - dW = 4\pi^2 m(2rf^2 dr + r^2 f df), \text{ or } dQ = fdJ$$

where $J = 4\pi^2 mr^2 f$, which is 2π times the angular momentum, or the action. The "capacity for energy of rotation at constant radius" is readily shown to be J; while that at constant centrifugal force is $-3J$.

Although designers of heat engines find the availability of heat, as related to the absolute temperature, an important factor, mechanical engineers have been able to regard energy of rotation as always completely available, however low the frequency. This difference does not form a defect in the analogy, but, on the contrary, arises because the earth is practically an infinite sink of rotational energy at zero frequency. For engineers who inhabited a rapidly rotating planet, or an asteroid of negligible moment of inertia, the availability of energy of rotation would become significant.

The possibility of analogies in mechanics to irreversible processes in thermodynamics is not discussed in this paper.

Two results of interest may be indicated, following from the above investigation:

(1) The passage from statics to dynamics is made in a novel manner, without the introduction of the concept of Newtonian time.[4] It appears profitable to study the consequences of the new approach.

(2) In a simple case, action is the analogue of entropy. In thermodynamics fluctuations have to be considered when entropy changes of the order of magnitude of Boltzmann's constant k are studied. From this point of view the quanta which come to view when changes in action of the order of Planck's constant h are dealt with need occasion no surprise.

It remains to find just how the introduction into dynamics of the "second law" stated above affects the logical structure of that subject. The new principle is to be substituted for older ones, presumably being equivalent to them as regards macroscopic phenomena, but not for microscopic. Finally it may be remarked that this paper employs a purely formal method which is alien to the thought of many physicists, but which nevertheless should be given latitude for development.

The writer takes this opportunity for expressing gratitude to his first instructor in thermodynamics, Professor William Francis Magie.

[4] In this connection it may be noted that P. W. Bridgman has shown that the concept of time is not necessarily fundamental in the definition of velocity (*The Logic of Modern Physics*, Macmillan, 1927, pp. 98, 99).

THE PHOTO-IONIZATION OF POTASSIUM VAPOR

By Ernest O. Lawrence and N. E. Edlefsen
Department of Physics, University of California

(Received August 28, 1929)

Abstract

Using a space-charge-neutralization method described in a recent publication the variation with wave-length of the ionization per unit light intensity B_ν in potassium vapor has been studied. B_ν exhibits maxima in the range 2100A to 3000A, one at the series limit, 2856A, and another at 2340A, the magnitude of the latter maximum being three times the former. A minimum value of B_ν occurs close to 2700A. Former results are shown to agree with the present much more accurate data though, because of the wide bands of wave-lengths used and the scantiness of observations, the earlier work failed to reveal the salient features here presented. The decrease of the ionization efficiency on both sides of the series limit is similar to the corresponding variation in caesium and rubidium and it seems probable, though not here proved, that the ionization by wave-lengths longer than the series limit is due to absorption of principal series lines. The increase of B_ν beyond the series limit has been attributed in the past to ionization of molecules. The present work shows that on this view the apparent molecular threshold occurs at 2700A and not at 2550A as estimated from earlier work. This fact in itself constitutes a serious objection to interpreting the observed variation of B_ν as a molecular phenomenon. It is pointed out that Williamson's observations of the emergent velocities of the photo-electrons show no evidence of molecular ionization involving dissociation of the molecule and ionization of one of the atoms. Also Ditchburn's observations of the continuous optical absorption due to potassium atoms agree qualitatively with the present results. It thereby appears probable that the observed dependence on wave-length of B_ν is an atomic property of potassium.

IT HAS been shown[1,2] that the photo-ionization per unit light intensity B_ν in potassium vapor increases on passing to shorter wave-lengths somewhat beyond the series limit. The experiments were beset with difficulties and only rather qualitative data were obtained. The results, however, were of considerable significance for they were not predicted theoretically and moreover bore no resemblance to the variation of B_ν in caseium and rubidium.[3,4] It was suggested[2] that the presence of an abundance of potassium molecules was responsible for the unexpected behavior, a view which was later given support by an investigation by Ditchburn[5] on the continuous optical absorption of potassium vapor. An adaptation of a quite different experimental method has made possible a much more quantitative study leading to results which, though qualitatively in accord with the previous observations, compel a revision of ideas and even suggest that the observed variation of B_ν is an atomic phenomenon after all.

[1] Williamson, Phys. Rev. **21**, 107 (1923).
[2] Lawrence, Phil. Mag. **50**, 345 (1925).
[3] Mohler, Foote and Chenault, Phys. Rev. **27**, 30 (1927).
[4] Lawrence and Edlefsen, Phys. Rev. **34**, 233 (1929).
[5] Ditchburn, Proc. Roy. Soc. **A117**, 486 (1928).

The experimental apparatus and technique were the same as used in a preceding study of caesium and rubidium.[4] Light from an iron arc source, resolved into wave-length bands by a Bausch and Lomb monochromator (0.2 mm slits) was separated into two portions by reflection and transmission through a quartz plate. The reflected portion passed into the photo-ionization tube and the transmitted portion was focused on a thermopile. The arrangement made possible simultaneous measurement of the photo-ioniza-

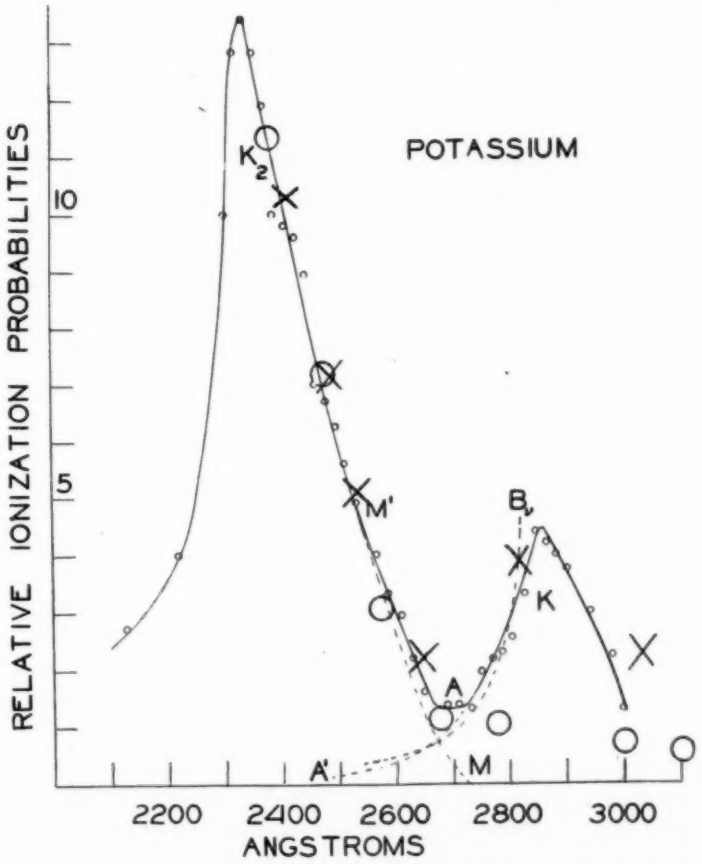

Fig. 1. The ionization per unit light intensity B_ν as a function of the wave-length. The small circles represent the data of the present experiments. The large circles represent earlier observations by Lawrence, and the crosses Williamson's recent data.

tion produced by and the intensity of the light. The photo-ionization tube was kept at a temperature near 210°C, being a temperature at which the quartz window was not discolored appreciably in a reasonable length of time though high enough to produce the requisite vapor pressure. The same care in distilling and purifying the potassium was used as in the preceding work.

The experimental results are embodied in the curve of Fig. 1. The ordinates are the relative values of B_ν for wave-lengths given by the abscissas.

The data were taken at 100A intervals over the whole range of wave-lengths, successive runs having their beginning at wave-lengths 20A apart. This was done to minimize systematic errors introduced by changing conditions in the photo-ionization tube which would have seriously altered the observed variation of B_ν with frequency had the observations been taken at successive intervals of 20A over the whole spectral range. The effects of changing conditions over runs involving 100A intervals were noticeable, though readily corrected for. The various runs were correlated and led to the composite data represented by the small circles of Fig. 1. To compare the results with former work the observations of Lawrence[2] have been plotted as large circles and the observations of Williamson[1] as crosses. Williamson's observations were made with a mercury arc and only his data corresponding to the wave-lengths of the more intense lines are recorded as significant. Lawrence's data represents the average effect of very wide bands of wave-lengths, a circumstance which, coupled with a scantiness of observations (due to the low intensity of the iron arc in the region of 2856A) near 2856A, obscured maximum of B_ν at the series limit. Thus it is seen that both sets of earlier observations are in qualitative agreement with the data represented here. Samuel's[6] observations also are in accord with the present data though his experiments were confined to the region of wave-lengths 2700 to 2900A.

The ionization efficiency B_ν exhibits two maxima, one (K) at the series limit, 2856A, and another (K_2) at 2340A. The variation of B_ν in the region of the series limit is quite similar to the corresponding behavior in caesium and rubidium and it would seem that the ionization by wave-lengths longer than the series limit involves absorption of the principal series lines as in the case of the heavier alkalis. The rate of decrease of B_ν to shorter wave-lengths beyond the limit is also very much the same as in the heavier alkalies down to approximately 2700A. This is illustrated by the dotted curve B_ν, being a plot of

$$B_\nu = \frac{\text{const.}}{(\nu - \nu_0)\nu^3}$$

which fitted so well the caesium and rubidium observations. Beyond 2700A B_ν rises rapidly to a maximum at 2340A falling off again at 2100A to a magnitude comparable to the 2700A minimum. B_ν at 2340A is about three times its value at 2856A.

Because of the similarity of the maximum $(K)_\nu$ of B_ν at the series limit to the observed variation of B_ν in caesium and rubidium the hypothesis naturally suggests itself that the second maximum (K_2) is due to ionization of potassium molecules. On this view the atomic part of the observed B_ν decreases for shorter wave-lengths to A (see figure) and probably along the extrapolated curve AA'. Thus molecular ionization presumably sets in at about 2700A, and the molecular part of B_ν increasing on passing to shorter wave-lengths to the maximum K_2 at about 2340A, and receding again beyond in the manner shown in the figure. Assuming the atomic extrapolation AA',

[6] Samuel, Zeits. f. Physik **29**, 209 (1924).

the molecular B_r curve would follow along the dotted curve $M'M$ yielding a threshold slightly above 2700A. The precision of the data introduces a probable uncertainty in this value of about 20A. The finite bands of wave-lengths also probably introduce a slight systematic error.

This hypothesis of molecules is not new and indeed a considerable amount of evidence has been adduced in its support. Originally, Lawrence[2] interpreted his rather surprising observations of B_r increasing on passing to shorter wave-lengths as a molecular phenomenon and suggested that an apparent change of slope at 2610A of the B_r curve marked a molecular photo-electric threshold. Later Ditchburn[5] carried out an experimental study of the continuous absorption of light in potassium vapor. He also concluded that a considerable part of the absorption was due to molecules and by taking observations at different vapor pressures he was able to separate the molecular and atomic contributions to the total absorption coefficient. He was handicapped in the analysis of his data by the unknown, though considerable, effect of the foreign gases necessarily present (pressures 3 cm to 70 cm). However, it appeared that molecular absorption abruptly increased on passing to shorter wave-lengths beyond 2550A. This result was regarded as a confirmation of Lawrence's earlier observations. Ditchburn[7] regarded the molecular absorption to be a process involving dissociation of the molecule plus ionization of one of the atoms. Ditchburn and Arnot[8] have recently shown that photo-ionization produces only atomic ions and therefore if molecules are ionized in appreciable amounts, the process must be just that. He observed, moreover, continuous absorption in the visible region of the spectrum which appeared undoubtedly to be due to molecular dissociation plus excitation of one of the dissociated atoms. On this view the data yielded for the dissociation potential of the potassium molecule the value 0.51 volts.

Thus the more accurate data of the present paper have weakened the strongest argument in favor of the molecular hypothesis. The apparent molecular threshold which was thought to be at 2550A and which was interpreted as measuring a dissociation potential of 0.5 volt comes more nearly at 2700A, corresponding to a dissociation potential of only 0.25 volt. Even with a dissociation potential of 0.5 volt Ditchburn[5] calculated that there were not more than 6 molecules present to every 10,000 atoms (at 550°K) and therefore to account for the results it was necessary to conclude that the absorption per molecule is about 10^4 times the absorption per atom. It is difficult to understand theoretically* such a relatively large molecular absorption coefficient. A lower dissociation potential indicating the presence of many fewer molecules greatly augments this difficulty.

However, there are other rather good reasons for believing that the dissociation potential is greater than 0.25 volt, and perhaps is nearer 0.5 volt. Carelli and Pringsheim[9] deduced a value for the heat of dissociation from observations of the variation of intensity of molecular fluorescence with

[7] Ditchburn, Cam. Phil. Soc. Proc. **24**, 320 (1928).

[8] Ditchburn and Arnot, Proc. Roy. Soc. **A123**, 516 (1929).

* We are indebted to Professor J. R. Oppenheimer for a discussion of this point.

[9] Carelli and Pringsheim, Zeits. f. Physik **44**, 643 (1927).

temperature when (1) the vapor was saturated and (2) when the pressure was kept constant. Assuming the fluorescence was proportional to the number of molecules present they obtained the values 0.63 volt and 0.53 volt. Ditchburn concluded that the systematic errors in Carelli and Pringsheim's method were such as to yield too high values and that 0.5 volt was a more was a more suitable estimate. Though it appears to the authors (further evidence favoring this view is given below) that the present results are concerned with the variation of the atomic B_r, it should be emphasized that that the hypothesis of molecules being responsible for the K_2 maximum does not imply that the molecular threshold at 2700A measures with accuracy the dissociation potential. The thermal energies of the molecules are of appreciable magnitudes and could shift the observed threshold considerably. A satisfactory estimate of the transition probabilities corresponding to ionization from various initial vibrational and rotational states to various states of the continuum, involving knowledge of the Franck-Condon potential energy curves, would be necessary to calculate the effect of the thermal energies on the observed threshold.

Williamson's[10] experimental study of the velocity distribution of the photo-electrons ejected from potassium vapor may be cited as excellent evidence favoring the view that the observed variation of B_r is an atomic phenomenon. He found that the maximum velocity of ejection for the wave-length 2399A to be even somewhat greater than that to be expected from ionization of the atom and there appeared to be no definite low velocity group which would result from molecular dissociation (dissociation potential 0.5 volt) and ionization. Though Williamson's work is very significant, his data are possibly not definite enough to settle the point. An accurate measurement of the energies of the ejected electrons of course would constitute crucial evidence for the correct interpretation of the photo-ionization process and therefore it is hoped that researches in this direction will be continued.

Ditchburn's[5] analysis of his data on the continuous optical absorption by potassium vapor possibly constitutes the best evidence in favor of the here observed B_r being an atomic phenomenon. By observing the variation of B_r at several pressures he was able to separate the molecular absorption from the atomic absorption and found that the atomic absorption was a maximum at the series limit, decreased to a minimum near 2700A and rose to a higher maximum again near 2400A. Thus his evaluation of the atomic absorption is quite in agreement with the present observations.

It appears, therefore, that the evidence supports the view that B_r for atomic potassium vapor does not decrease with wave-length monotonically beyond the series limit as is the case for caesium and rubidium, the continuous absorption beyond the Lyman and Balmer limits and in the x-ray region. One of us (N. E. E.) expects to carry through the quantum mechanical calculation of this effect.*

[10] Williamson, Proc. Roy. Soc. **A114**, 796 (1928).

* A similar calculation for the photoelectric effect in lithium has been made by Hargreaves, Proc. Camb. Phil. Soc. **25**, 75 (1929).

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Scattering of Light By Kerr Cell

The amount of light from a mercury arc scattered at small angles in its passage through a parallel plate condenser, containing water as its dielectric, was investigated. The intensity of the light scattered at small angles to the direction of the directly transmitted beam, when a high frequency field of one meter approximately was impressed on the plates of the condenser by a short wave-length oscillating circuit, was found to be comparable in intensity to the radiation falling on the cell. The spectrograms taken in the ultraviolet region from 3000A to 2500A of the light scattered at angles from 1° to −1° with respect to the direction of the primary beam indicated that all the light passing through the cell had been scattered. For lower frequencies, order of 6 meters wave-length, the amount of scattered light depended on the wave-length of the light.

The light scattered by the Kerr cell showed a change in wave-length towards the red of 0.06A, the same as that reported by the writer (Phys. Rev. **33,** 279 and 640, 1929) for certain lines of the mercury and iron arc, respectively, when the high frequency field impressed on the cell had a wave-length of 6 meters. All the mercury lines, so far observed, 4358, 5460 and 5769 respectively, show this red displacement when the high frequency field impressed on the Kerr cell has a wave-length of one meter.

The observations on the light scattered at small angles by the cell indicate that only the light which has been scattered by the cell suffers the displacements towards the red. The difference in the behavior of the lines for lower frequencies of the field impressed on the cell, is due to the marked difference in the ratio of the intensity of the scattered light to the primary beam, entering the cell, for the different lines.

A. BRAMLEY
Bartol Research Foundation
Swarthmore, Pa.
September 14, 1929.

The Symmetry of Nuclear Wave Functions

Dr. F. Rasetti, working at these laboratories, has clearly shown by his experiments on the Raman effect in nitrogen that the even rotational states of the nitrogen molecule have a greater weight than the odd rotational states in contradistinction to the behavior of the hydrogen molecule. Heitler and Herzberg[1] have pointed out that this is a very surprising result because the nitrogen nucleus contains an even number of protons and an odd number of electrons so that, no matter what statistics protons satisfy, we should expect the wave functions for nitrogen nuclei to be antisymmetric in those nuclei. Assuming that Dennison's theory of the rotational specific heat of hydrogen and Hori's analysis of the band spectrum of hydrogen prove that hydrogen nuclei have antisymmetric wave functions there is apparently no path to take but suggest, as Heitler and Herzberg have done, that the symmetry properties of nuclei do not depend upon those of the electrons supposedly contained in them. This would introduce many theoretical difficulties.

[1] Heitler and Herzberg, Naturwissenschaften **34,** 673 (1929).

However, the writer has shown[2] in a brief note that a complete analysis of the symmetry properties of symmetrical diatomic molecules shows that Dennison's theory and Hori's experimental work are evidences that protonic wave functions are symmetric, that is, protons satisfy the Einstein-Bose statistics. If this is so, the same analysis applied to the nitrogen molecule, making the natural assumption that the nitrogen nuclei satisfy the Fermi-Dirac statistics on account of the odd electron, leads one at once to expect Dr. Rasetti's experimental results. As a matter of fact the writer predicted this result to Dr. Rasetti before he knew of the results of the photographs.

Perhaps there is one confusing point in the paper showing that protonic wave functions are symmetric. ψ_e as defined in that paper was stated to be unchanged by simultaneously interchanging the nuclei and electrons of the molecule there considered. The confusion seems to arise from the apparent difficulty in choosing the coordinate system of rest of the weak magnetic field quantizing the spins of the electrons. Evidently the magnetic field can be specified in any coordinate system but it must be regarded as a moving field in all systems but those at rest to the system in which the electronic coordinates are specified. In this case, such a coordinate system is determined by the nuclei and rotates with the molecule. A little consideration will show that by interchanging the nuclei, the coordinate wave functions of the electrons in a basic Σ_1 state of a molecule are unchanged while the signs of the spins are changed because the quantizing magnetic field is first regarded in a positive direction and then in a negative direction. The interchange of the electrons which also involves the spins then restores the wave function to its original sign. Quantizing the electronic spins in a field fixed in space, that is a moving field as far as the molecule is concerned, will for an individual molecule sometimes find the electron spins parallel and sometimes antiparallel. But for an assembly of molecules it will have an equal probability of finding electron spins oriented with or against the field.

BENEDICT CASSEN
California Institute of Technology,
Pasadena, California
September 17, 1929.

[2] Cassen, Proc. Nat. Acad. Sci. **15,** 29 (1929).

The Heat of Dissociation of Oxygen and of Nitrogen

Two communications in the Physical Review of September 1 seem to call for brief comment. The first is a letter by L. S. Kassel (page 817) in which, from work on the decomposition of ozone, it is deduced that the heat of dissociation D for O_2 lies between 5.0 and 5.5 volts, as contrasted with the Birge and Sponer value of 7.0 volts. In a paper to be read September 24 at a symposium of the Faraday Society, I am presenting a new method for extrapolating vibrational energy curves of molecules (ω_n:n) in cases where these are not linear. Using new data by Rasetti and by Fesefeldt, I find the ω_n:n curve for the normal state of O_2 is definitely *not* linear and cannot give value of D as large as 7.0 volts. From this it follows that molecules in the upper "B" level of O_2 dissociate into one excited and one normal atom, in agreement with Herzberg's theoretical remarks, and that the Birge and Sponer value of 7.0 volts is too large by just the amount of this atomic excitation. My extrapolation indicates that D should be between 5.6 and 6.5 volts, with 6 volts as a most probable value. The resulting atomic excitation, one volt, is in conflict with values of about 2 volts, calculated by Bowen and by Kaplan (Phys. Rev. **33,** 638 1929) for the ^1D metastable level of the oxygen atom. Hence it may be said that the correct value of D for O_2 is at the moment rather uncertain.

The second communication is by L. A. Turner and E. W. Samson (page 747), in which the 0–1 negative band of nitrogen is found to be excited at 19.0 volts, in contrast to Sponer's value of 19.6 volts. These writers quote me as obtaining 3.9 volts for the D of the upper (excited) level of N_2^+. I gave 3.9 volts as an upper limit, not as a most probable value. Using the new method of extrapolation I now find 3.7 ± 0.1 volts as the most probable value. This is discussed in my Faraday Society paper. The well-known process used by Turner and Samson then gives 8.84 volts for the D of N_2, if Sponer's 19.6 volts is correct, or 8.24, if their new 19.0 volt value is correct. Turner and Samson note that if

they have N_2 molecules present in the first vibration state, their 19.0 volt value will be too low by the amount of this excitation (0.29 volts). It is quite true that the Boltzmann distribution gives only a negligible number of such excited molecules, at the effective temperatures used, but attention should be called to the fact that the vibrational levels of the normal state of symmetrical molecules are strictly metastable, and the number of molecules in such states may therefore be far in excess of that given by the Boltzmann factor. Unpublished work by C. A. Pulskamp, of this laboratory, shows that this is indeed true for the normal level of O_2. Hence the Turner and Samson value of D for N_2 may well be 8.5 volts or even higher. On the other hand, direct experimental values of the ionization potential of N_2 run as high as 16.9 volts, leading to D as high as 9.24 volts. I think that all we may conclude is that the heat of dissociation of N_2 is in the heighborhood of 9 volts.

RAYMOND T. BIRGE
University of California
September 17, 1929.

The Temperature of the Planets

Recent measurements with a thermocouple by Coblentz, Lampland, Pettit, Nicholson and others of the temperatures of the planets have yielded temperatures below 200° Kelvin for Jupiter, Saturn, Uranus, Neptune and the night side of Mars. The dayside of Mars was found to be around 300° Kelvin. These results have been regarded by some writers to mean that Mars has an enormous diurnal temperature fluctuation and that the outer planets are very cold. Such inferences are perhaps doubtful because the atmosphere of a planet may be cold and the surface of the planet warm. For example, in the case of the earth a detailed calculation led to the following statement (Maris, Terr. Mag. and Atmos. Elec. **33,** 233 (1929)): "An observer on Mars measuring the temperature of the Earth with a telescope and sensitive thermocouple would find radiation from the night equator representing a temperature of a little over 205° Kelvin, the temperature at the base of the stratosphere, plus a small amount of radiation from the warmer strata below; from the night poles he would receive radiation representing a temperature of 230° Kelvin, the temperature of the stratosphere in this region." The calculation indicated that the day side of the earth would radiate energy characteristic of temperatures as high as 350° Kelvin if the air were dry, as over a desert, and of somewhat lower temperatures if the air were humid.

Therefore it would seem that the atmosphere of a planet should be considered in estimating planetary temperatures from thermocouple observations. Explanations of the low densities of the outer planets will depend to some extent upon what temperatures are assigned to the planets.

E. O. HULBURT
Naval Research Laboratory,
September 17, 1929.

Chemical Heats of Activatian

Two methods of attack on the quantum mechanical problem of chemical heats of activation have been suggested. (Langer, Phys. Rev. **34,** 92 (1929); London, Zeits. f. Electrochem. **35,** 552 (1929). In this note I should like to advance a third, which should prove powerful, as it has already led to a qualitative success from a semi-classical point of view. The method is a direct application of the Franck-Condon considerations (Franck, Trans. Faraday Soc. **21,** 536 (1926); Condon, Phys. Rev. **28,** 1182 (1926); Proc. Nat. Acad. **13,** 462 (1927); Phys. Rev. **32,** 858 (1928)) to the case of a radiationless transition, in much the same manner as was used by Franck and Sponer (Göttinger Nach. 241, 1928). To investigate the HI thermal decomposition, potential energy curves of I_2, H_2, and HI were plotted, using Morse's (Morse, Phys. Rev. **34,** 57 (1929)) function. In the "zero" approximation the shape of one HI curve may be considered as not being deformed by the proximity of a second HI molecule. A one-dimensional collision was then pictured by drawing a second curve at an appropriate distance from the first. The allegiance of H_a in the first molecule, H_aI_a, could then change from I_a to H_b and the allegiance of I_b in the second molecule, H_bI_b, could simultaneously change from H_b to I_a by a radiationless trans-

fer if no change in position were necessary to bring about the fulfillment of the energy equation,

$$\begin{aligned} x + y + Q &= a + b \\ \mathrm{HI} + \mathrm{HI} &= \mathrm{H_2} + \mathrm{I_2} + Q \end{aligned}$$

where the letters represent the vibrational energies of the respective molecules written below them and where Q is the heat of reaction. The postulate was laid down that translational energy does not enter into the reaction mechanism (as is quite often assumed) and was justified by the work of Beutler and Josephy (Naturwissenschaften **15**, 540 (1927); Zeits. f. Physik **53**, 747 (1929)); Webb and Wang (Phys. Rev. **33**, 329 (1929)); and Kallman and London (Naturwissenschaften **17**, 226 (1929); Zeits. f. Phys. Chem. **28**, 207 (1929)). The heat of activation is then,

$$A = x + y + F$$

where F is the (repulsive) energy necessary to bring the molecules together to the position at which that particular collision was considered to occur. Over one hundred cases were calculated graphically and it was found that the smallest value of

$$A' = x + y$$

came out to be 50 k. cal. The difference between this value and the experimentally observed heat of activation (44 k. cal.) is of the correct order of magnitude for the attractive forces existing between the molecules. (The heat of sublimation is about 5.5 k. cal.)

The possibility of the strict application of the quantum mechanics to this working method is being further investigated. The detailed description of the above results has been submitted for publication to the Journal of the American Chemical Society.

DONALD STATLER VILLARS
School of Chemistry,
University of Minnesota,
September 23, 1929.

BOOK REVIEWS

Experimental Optics. ALBERT F. WAGNER Pp. 203, figs. 117. John Wiley and Sons, New York, 1929. Price, $3.25.

This laboratory manual is based on a course given at the U. S. Navy Postgraduate School, the purpose of which is to give the junior officers such knowledge of optics as is necessary for the inspection of optical instruments. It is therefore natural that the greater part of the text is on geometrical optics. Practical methods are given for the measurement of focal lengths, magnifying powers, and aberrations of lenses and various optical systems. A chapter on microscopes is included.

There are a few well chosen experiments in physical optics of which four experiments covering eight pages deal with interference and diffraction. It is suggested that there is a connection between resolving power and magnification in the practical use of a telescope, but the reasons for this are not given. There are three pages of a most elementary nature on polarized light. Eight pages are devoted to spectroscopy of the infra-red and ultra-violet. There are also fourteen pages on elementary photometry, which include measurements of illumination and brightness with the Macbeth illuminometer. Omissions that might be noted are heterochromatic photometry and angular distribution of light flux. There are seven pages on spectrophotometry, and twenty-four on refractometry. The author fails to give a clear and accurate method for adjusting the spectrometer, partly because the procedures to be followed with and without a Gauss eyepiece are given simultaneously. The appendices contain various useful laboratory information including chemical formulae for silvering, photography etc., and tables of optical and mathematical constants.

This text should be of interest to all serious students of optics chiefly because of the great amount of practical information it contains on tests and measurements of lenses and optical instruments.

J. VALASEK

Numerical Tables of Hyperbolic and Other Functions. J. W. CAMPBELL. Pp. 76, 14×21 cm. Houghton Mifflin Company, Boston, 1929. Price $1.25.

As stated in the preface the main purpose in compiling these tables has been to provide tabular values of hyperbolic functions in a form readily accessible for practical use.

Table I gives $\sinh x$ and $\cosh x$ from $x=0.000$ to 3.000 to four decimals and from $x=3.000$ to 8.000 to five significant figures. Table II gives $\tanh x$ from $x=0.000$ to 1.800, 1.80 to 3.00 to four decimals. Table III gives $(\sinh x)/x$, $(\cosh x-1)/x$, Table IV $(\cosh x)/x$. In addition Table XIV gives $\sinh x$ and $\cosh x$ from 0.00 to 2.50 to seven decimal places and from 0.0000 to 0.0250 to seven decimal places. Other tables give values of the trigonometric functions for decimal values of the argument and for degree values, $\log_{10}x$, and $\log_e x$ from $x=1.00$ to 10.00. There are included tables of x^2, x^3 and $1/x$, for $x=10$ to 100 to four significant figures.

Use of the tables is illustrated in the appendix in connection with problems of the catenary, electric transmission lines and the solution of cubic equations.

The tables are serviceably bound.

JOHN T. TATE

Einführung in die Wellenmechanik. J. FRENKEL. Pp. 317, 10 figs. Julius Springer, Berlin, 1929. Price unbound, RM 11.

This book can perhaps be best reviewed by comparing it with Sommerfeld's *Wellenmechanischer Ergänzungsband* which has already attained a wide circulation among American physicists. It is quite similar in its general scope but perhaps treats a wider range of topics. In view of the far-reaching consequences of quantum mechanics for physics, chemistry and philosophy, it is certain that the next few years will see the publication of a large number of

introductory books on this subject. The preface says that the book "sets itself the problem of presenting in the simplest possible form the very simple things which are the essence of the new microphysics." It is quite successful in doing this. The first chapter introduces wave mechanics by a thorough discussion of the wave-particle dualism in both light and matter. The second develops the equations, including a discussion of Dirac's spin equations along the lines of Frenkel's own work. The third works out the general theory of the perturbation of atoms by light waves, radiationless transitions and the exchange phenomenon. The fourth details the application of the theory to special problems.

I think it worth while to quote here from p. 37 from the section on the probability concept and the principle of causality because this topic occupies such a central place in discussion today:

"Independently of whether one regards the matter waves merely as probability waves or ascribes to them a physical reality, one must regard the physical happenings, when treated from a corpuscular standpoint, as undetermined. The earlier deterministic mechanics knew only the probabilities 1 and 0. It concerned itself with the study of those events whose probability is equal to 1, by means of integration of certain equations of motion with regard to exact initial conditions. The new mechanics knows no exact initial conditions. The classical alternative—either necessary or impossible—it does not know. For it *anything* is to be regarded as *possible* . . . . . Correspondingly the new mechanics does not concern itself with the discovery of certain events having a given probability, but with the study of the probability of all possible events."

The book is nicely printed, in the same style as Frenkel's "Elektrodynamik." As to the binding, one cannot say since the thrifty publisher sends an unbound copy for review!

E. U. CONDON